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AND  
DEPARTMENT OF SCIENTIFIC AND  
INDUSTRIAL RESEARCH

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Technical Records of  
Explosives Supply

1915-1918

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No. 5  
MANUFACTURE OF SULPHURIC ACID  
BY CONTACT PROCESS

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Department of Scientific and Industrial Research,  
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October 1921

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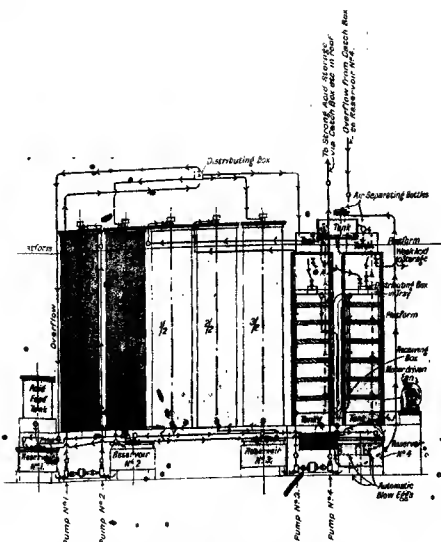
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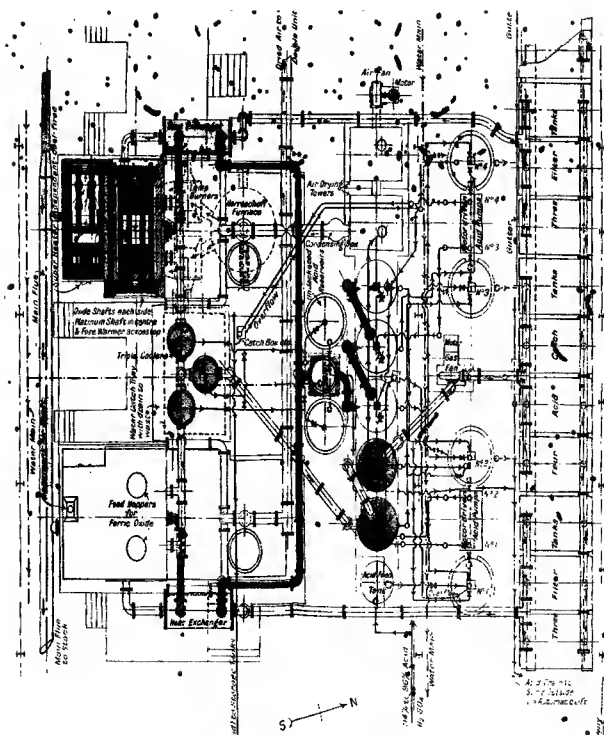
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INTERCONNECTING ACID PIPES & PUMPS NOT SHOWN.



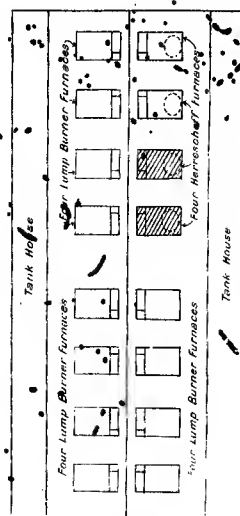
(PUMP PIPING & GAS FAN NOT SHOWN.)



PLAN  
OF SECOND HERRESCHOFF DOUBLE UNIT

### DIAGRAM OF CONNECTIONS

Scale: 1" = 6 feet



50 Feet = 1 inch

## PIPING

- |                               |        |
|-------------------------------|--------|
| 1 <sup>st</sup> Flow Hot Gas  | Yellow |
| 2 <sup>nd</sup> Flow Hot Gas  | Green  |
| 2 <sup>nd</sup> Flow Cold Gas |        |
| Acid                          | Black  |
| Water                         | Blue   |
| Dried Air                     | White  |



## INTRODUCTION

In the early days of the war the demand for high explosives involved the use of quantities of strong sulphuric acid and "oleum" far in excess of the producing capacity of the country. The Government has, consequently, to build plants to make sulphuric acid by the contact process. The first to be erected were on the Mannheim system, from plans supplied by Messrs. Kynoch. Later, plants designed by Mr. K. B. Quinan and his staff at Storey's Gate, using the Grillo contact mass, were constructed, and in these plants the largest amount of oleum was produced.

Tentelew plant was also operated by the Department of Explosives Supply in the Pembrey factory originally erected by Messrs. Nobel and subsequently taken over by the Government. The working costs and efficiencies of these processes are set forth in the Second Report of Costs and Efficiencies for H.M. Factories Controlled by Factories Branch, Department of Explosives Supply, and *see also* Report of the Statistical Work of the Factories Branch.

The distinctive characteristic of the Mannheim process is that the conversion of the sulphur dioxide into the trioxide is brought about in two stages by employing two catalysts: ferric oxide and platinum. The use of ferric oxide diminishes the quantity of platinum required and thus reduces the capital cost of the plant. In the Grillo and Tentelew processes only platinum is used as catalyst.

In the Mannheim and Tentelew plants the finely divided platinum supported on asbestos in the form of mats or fibre, whereas, in the Grillo, calcined magnesium sulphate in the form of coarse grains is used as the carrier for the platinum.

In all the processes it is essential to purify the gases thoroughly before letting them come in contact with the platinum, as certain bodies, even when present in minute quantities, such as arsenic, selenium, fluorine and other halogens seriously impair, or even destroy, the activity of the platinum, and the conversion of sulphur dioxide to trioxide will diminish or cease altogether. Should such "poisoning" occur the contact mass must be withdrawn and treated to remove the poison, and then returned to the plant or else replaced by fresh contact mass.

The purification of the gases is therefore, all-important. When sulphur is used as the raw material it rarely introduces arsenic itself, but nevertheless the contact mass may suffer from arsenic poisoning due to arsenic picked up from the iron used in the construction of the plant, unless certain precautions are observed.

Iron pyrites was used in the Mannheim and Tentelew plants, and sulphur for reasons given later in the Grillo.

## MANNHEIM PROCESS

### SECTION 1

#### MANNHEIM OLEUM PLANT

~~General outline and~~ description of plant.—The Mannheim plant produces oleum by the absorption of sulphur trioxide in sulphuric acid, the sulphur trioxide being made by the catalytic action first of iron oxide, and later of platinum contact mass on sulphur dioxide gas, produced by the burning of pyrites containing about half its weight of sulphur in the form of iron sulphide.

The Mannheim oleum plant comprises :—

- (a) Pyrites store;
- (b) Pyrites crusher plant;
- (c) Mannheim oleum plant proper, each double unit capable of producing about five tons of  $\text{SO}_3$  per 24 hours. At Queen's Ferry eight of these double units are arranged for the burning of lump pyrites. The remaining two double units are of the Herreschoff type for burning pyrites "fines." Each unit has its own iron oxide conversion shafts, preheaters, and platinum contact shaft. Two of these single units work together (forming a double unit), with their necessary coolers, absorption towers, acid mist catchers, &c. There are in addition :—
  - (d) Store and bins for burnt iron oxide ore;
  - (e) Storage tanks for the storing of oleum; and an
  - (f) Oleum export building.

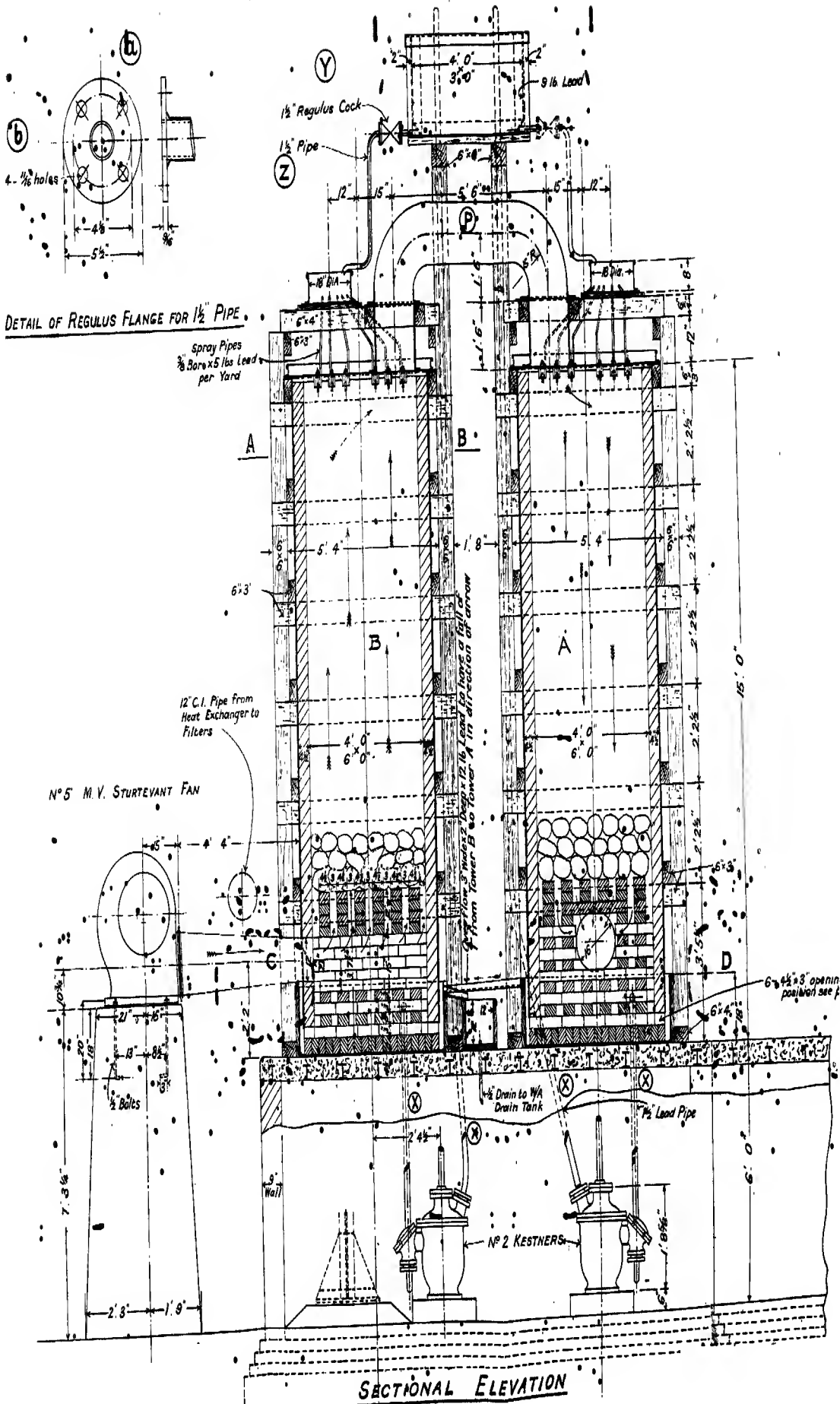
#### PYRITES STORE

This is a steel frame structure 205 feet long  $\times$  85 feet wide, having a concrete floor. Three lines of 4 feet  $8\frac{1}{2}$  inches gauge factory railway enter the building, and are supported on brick piers.

#### CRUSHER PLANT

This consists of a crusher plant building, containing a 21 inch  $\times$  10 inch Broadbent patent improved Blakestone breaker, to break eight tons of iron pyrites per hour from 9 inch lumps to pass through  $2\frac{1}{2}$  inch rings, driven by a 20 h.p. motor, and one set of geared crushing rollers, 8 inches diameter  $\times$  10 inches face, for pyrites from 1 inch ring to  $\frac{3}{8}$  inch, driven by a 20 h.p. motor. The crushed pyrites is conveyed by a belt conveyor to a screening house, fitted with a revolving screen, or trommel, 3 feet diameter, 15 feet 8 inches long, which sorts the crushed pyrites into  $2\frac{1}{2}$  inch, 1 inch and  $\frac{3}{8}$  inch sizes. The trommel is driven by a 20 h.p. motor. The three different sizes of screened pyrites are conveyed into three separate bins, which are fitted with hoppers, under which is a narrow gauge track on which run bogies,







These are weighed on a 30 cwt. platform weighing machine, and from thence the bogies can be run directly to the burners in the Mannheim plant.

#### DESCRIPTION OF OLEUM PLANT

The oleum plant proper is housed in a steel frame building all under one roof (Fig. 1). The plant inside the building consists of ten double units or sections. Eight of these are for burning lump pyrites of an average size of 2 inch ring. The remaining two double units are each of the Herreschoff type for burning pyrites "fines." Each single unit is built in brickwork, firebrick lined, and the whole enclosed in a mild steel casing of about  $\frac{1}{2}$  inch plate. This casing encloses the burners, oxide shafts, forewarmers and platinum contact shaft. Built against each casing at the back is a brickwork chamber enclosing the superheater, which is fired by a separate coke fire.

**Air drying towers (Fig. 2).**—As it is essential to avoid, as far as possible, moisture entering the system with the gases, the air for combustion of the pyrites is first dried in air-drying towers. Two air-drying towers are provided for each two double units. Each air-drying tower consists of a lead box supported by timber framework (inside dimensions, 4 feet  $\times$  6 feet  $\times$  15 feet high), lined with unjointed brickwork. A brick grid floor supports the coke filling. The atmospheric air is driven into the bottom of the tower by a No. 5 Sturtevant fan driven by a 6 h.p. motor. Acid is circulated to the top of the towers by centrifugal pumps delivering about six tons of acid per hour in each tower. The two towers are connected in series. The air after leaving the second or strong tower, is conveyed in a gas main, and thence, by distributing pipes, to the 24 burners of the two double units.

**Lump burners (Fig. 3).**—Each single unit consists of six burners (two sets of three placed back to back) of the usual type. Each burner has a grate area of 20 square feet, and is capable of burning about half a ton of pyrites in 24 hours. The bed of the burner is formed of square section grate bars which can be revolved by means of a key, so as to enable the burnt ore to be dropped into hoppers underneath. Every three burners, which are separated from one another by a low brick wall, have a common flue which leads the gases into the base of the oxide conversion shaft. The burners are totally enclosed, the air for combustion being supplied under a slight pressure from the air-drying towers by means of pipes leading under the grates.

**Oxide shafts (Fig. 4).**—Each double unit has four oxide conversion shafts (one to each three burners). Each oxide shaft consists of a square chamber with an inside sectional area of 21 square feet. The lower 10 feet is reserved for iron oxide packing, but is never filled more than 7 feet 6 inches under normal conditions. The upper 10 feet contains the hopper for charging fresh iron oxide and the forewarmer pipes used for heating regeneratively the gases going to the platinum converter shaft. The iron oxide filling is supported on iron bars similar to those

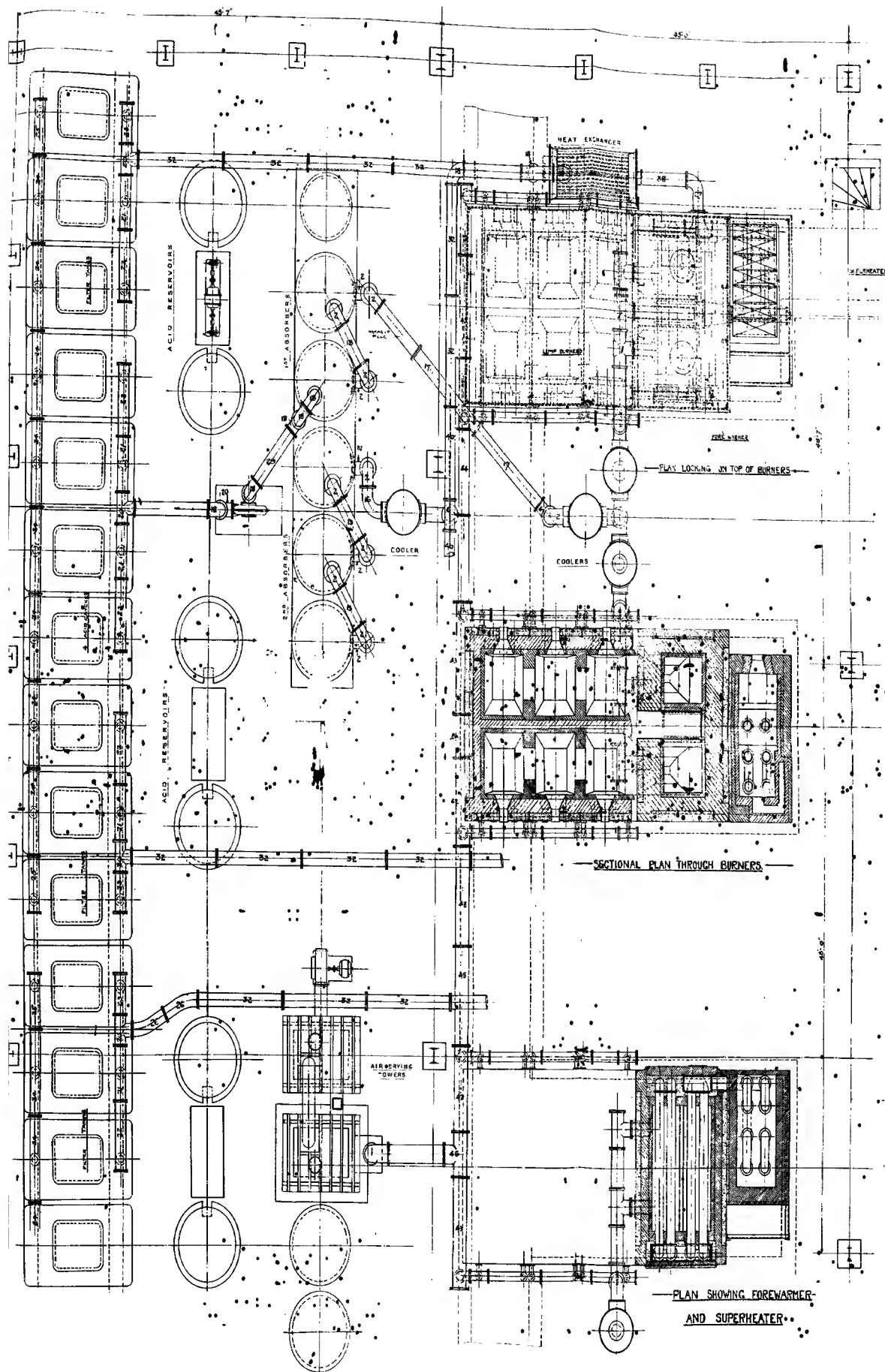
in the pyrites burners. The burnt ore can be shaken out from time to time into hoppers which deliver the same into cellars below the floor level.

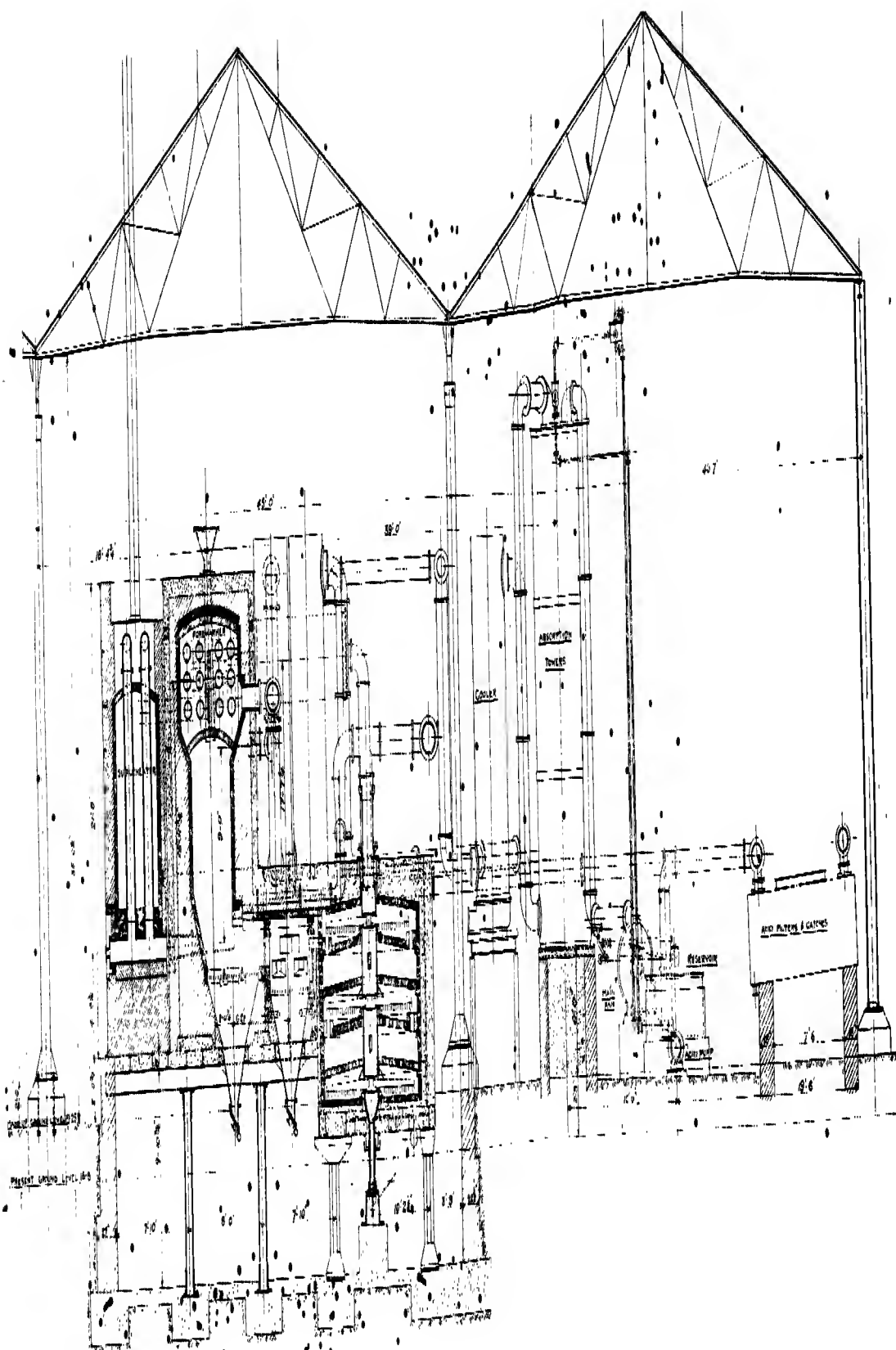
**Oxide shaft coolers (Figs. 3 and 4).**—The gases from the two oxide shafts of one unit, which have been partially cooled in passing over the forewarmer pipes, enter the base of a cylindrical steel cooler 3 feet 7 inches diameter, 16 feet 5 inches high, containing four circular baffle plates. The cylinder sits on a lead saucer and the gases passing up inside are cooled by water distributed from the top over the exterior surface of the cylinder. The gases from two of these preliminary cooling towers (coming from the four oxide shafts of a double unit), unite, and pass through a third final cooler of the same type.

**Absorption towers (Figs. 3 and 4).**—The gases leaving the oxide shaft coolers are conveyed by a 14 inch cast-iron gas main to two absorption towers working in series, for the purpose of absorbing, by means of sulphuric acid, the  $\text{SO}_3$  produced in the oxide shaft. There are five absorption towers to each double unit; the functions of the remaining three towers will be explained later. Each absorption tower consists of a mild steel cylindrical shell, 5 feet diameter  $\times$  24 feet high, built up in sections jointed with asbestos rope, and lined with acid-proof bricks of about 8 inches  $\times$  6 inches  $\times$  3 inches thick, jointed in acid-proof cement. A cast-iron grid resting on angle pieces riveted inside the shell, at a height of 2 feet 8 inches from the bottom, supports about 30 tons of quartz filling. Additional support to the cast-iron grid is provided by a centre pillar resting on the base of the tower. At the top of the tower is a cast-iron acid distributing plate.

**Purification system.**—The gases of the double unit, after passing in series through two absorption towers, are pulled through a Kynoch fan, driven by a 6 h.p. motor. From the fan they are driven through a purification system, consisting, for each double unit, of four acid catchers and six filters (three for each side of the acid catchers) (Figs. 3 and 4). The acid catchers consist of steel boxes, 11 feet 6 inches  $\times$  6 feet 7 inches  $\times$  4 feet 1 inch high, filled with graded quartz, supported on a steel grid. The gases enter at the top, pass down through the filtering medium into the bottom grid past a baffle, and up again and out of the box. The four acid catchers are connected in parallel to both an incoming and outgoing gas main. From the acid catchers the gases pass in parallel through six filter boxes of similar construction, but packed with quartz on the grid, then slag sand with a covering of 3 inches of a mixture of asbestos fibre and lime.

**Heat-exchanger (Fig. 3).**—The gases of a double unit, after leaving the purification system, divide, one-half of the gas passing through the heat exchanger of one unit, and the other half passing through the heat exchanger of the other unit. The heat exchangers are identical in construction with those at the Grillo plant, which are described in detail in the Grillo plant section. The cold gases flow through the tubes of the heat exchanger, and are heated in their passage by the hot gases





SECTIONAL ELEVATION THROUGH HERRESHOFF

FURNACES

FIG. 4.1

## DESCRIPTION OF PLANT

from the platinum conversion shaft, which circulate around the outside of the tubes.

**Forewarmer (Figs. 3 and 4).**—The partially-heated gases are still further heated by passing through a series of 12 horizontal pipes, jointed together by double bends, each pipe being 10 inches diameter and 12 feet 6 inches long, with a total outside heating surface of 80.4 square feet. The hot gases passing up the oxide shaft circulate around the outside of these forewarmer pipes.

**Superheater (Figs. 3 and 4).**—The hot gases from the forewarmer are finally further heated in a coke-fired "superheater" to an optimum temperature for conversion in the platinum shaft. Each single unit has one superheater, consisting of six vertical pipes and headers, heated by a coke fire. The outside heating surface of the pipes is about 10 square feet. The furnace is of ordinary brick, with firebrick lining, 6 feet 10 inches  $\times$  13 feet 10 inches wide  $\times$  21 feet 8 inches high.

**Platinum contact shaft (Fig. 5).**—The gases leaving the superheater pass up through the platinum contact shaft (one for each single unit). The platinum contact shafts are made of cast-iron, built up in sections, one on top of the other, to form three ovens, each 12 inches deep  $\times$  1 foot 3 inches long  $\times$  2 feet 3 inches wide. Inside each oven is placed a cast-iron frame, into which is fitted ten asbestos platinised mats separated by wire gauze. The cast-iron frames are conveniently constructed for clamping the four edges of the mats together, the whole being clamped tightly with iron bolts. Each oven is fitted with a cast-iron door 30 inches long  $\times$  14 inches wide, for the purpose of changing the mats when necessary.

**Final absorption (Figs. 5).**—The gases, after passing up through the platinum contact shaft, are heated by the chemical reaction taking place, and some of this heat is usefully employed in the heat-exchanger, as mentioned before. These gases from each double unit, after leaving their respective heat exchangers, join at a "T" piece and pass up through a vertical cooler, so called "platinum" cooler, similar in construction to the oxide shaft coolers previously described. After leaving this cooler, the gases from the double exit pass through three absorption towers in series. These towers are placed alongside, and are similar in construction to, the absorption towers described for the absorption of the  $\text{SO}_3$  converted in the oxide shaft. From the last tower the gases pass to a chimney exit into the atmosphere.

**Circulation system.** For the purpose of circulating acid down the five absorption towers of each double unit, there are provided, on the ground floor, four mild steel acid reservoirs 6 feet diameter inside  $\times$  3 feet high, three of which are water-jacketted and one without water jacket. Four 1½ inch centrifugal Kynoch acid pumps, driven in pairs by 3-h.p. motors, are provided for circulating the acid from the reservoirs to the top of the five towers. One mild steel feed tank, 5 feet diameter by 5 feet high, constructed on a brick pier, at one end

of each battery of absorption towers, of a double unit, serves to provide lead acid by gravity to No. 1 reservoir.

**Drip acid.**-- A number of small tanks are provided for collecting drip acid from the acid catchers, filters, coolers, fans, etc. Puhle air lifts raise this acid to a common lead launder, which conveys the acid by gravity to a storage tank.

**Herreschoff burners (Figs. 4 and 5).**-- In addition to the eight double units of lump burners already described, there are two double units of the Herreschoff type for burning pyrites "fines." These Herreschoffs are of the ordinary standard type, with five shelves. The "fines" are fed from hoppers overhead by means of worm feed, and are distributed over the top shelf by revolving arms fitted with teeth. The teeth of the first arms are so arranged that they pass the "fines" to and over the outer periphery of the circular shelf. On the second shelf the teeth draw the "fines" toward the centre, where they fall on to the third shelf, and so on over the five shelves, the residues finally falling into a hopper below.

The vertical hollow air-cooled central shafts of the four Herreschoffs to which the distributing arms are attached, are slowly rotated by geared attachment to a central line shaft driven by a 10 h.p. motor. The cooling of the central shaft is brought about by the cold air from the air-drying towers, which passes downward through the hollow shaft, and outward through small openings in the shaft to each shelf.

Each of the four Herreschoffs takes three tons of pyrites "fines" per 24 hours. As the Herreschoffs do not heat the gases sufficiently for good conversion in the oxide shaft, a small lump burner is constructed alongside each Herreschoff, the hot gases from which, mixing in a common flue with the comparatively cold gases of the Herreschoffs, bring the temperature of the mixture up to an optimum condition for oxide conversion.

Inasmuch as there are two oxide shafts to each Herreschoff burner, there are two lump burners to each Herreschoff burner, placed back to back, of similar construction to those previously described, each burning half a ton of lump pyrites per 24 hours.

Each double unit Herreschoff, with its two Herreschoff burners and four lump burners, has four oxide shafts, five absorption towers, similar coolers, acid reservoirs, pre-heaters, etc., as have already been described for the double lump burner unit.

#### OPERATION OF THE PLANT

**Crushing pyrites.** When the whole of the Mannheim plant is being operated, the two Herreschoff burners are only capable of taking about half the "fines" produced by the mechanical crushing plant, which produces about 32 per cent. of "fines" (depending on the ore). It is found, therefore, economical to break the ore by hand, which reduces the percentage of "fines" to about 10 per cent.

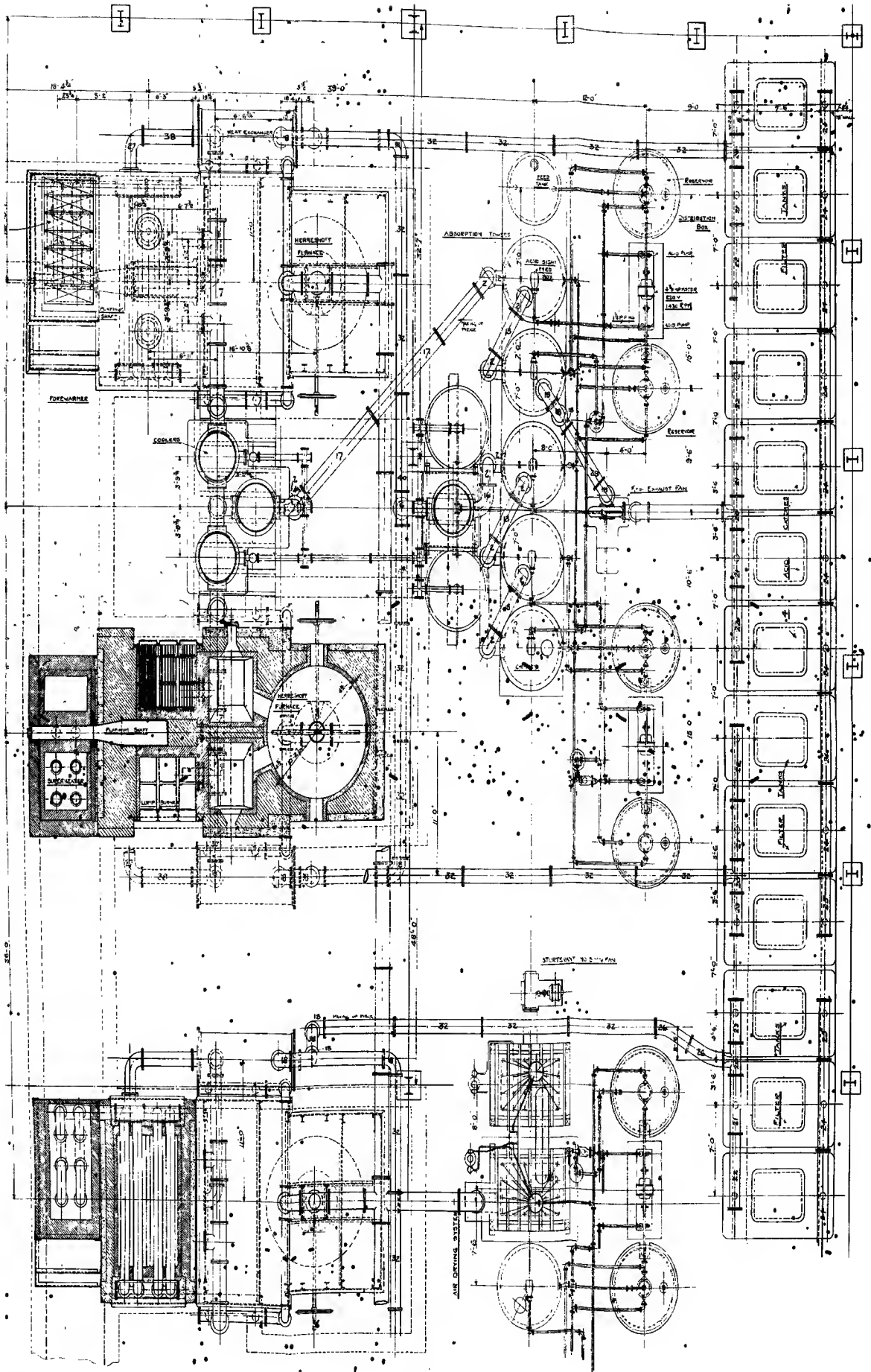


FIG. 5.

Weighed charges of the ore are trucked in bogies to the Mannheim burners, lump ore *via* an 18 inch gauge track on the floor level to the lump burners, and "fines" *via* an electric hoist and overhead 18 inch gauge track to the hoppers of the Herreschoffs. Each bogie holds 15 cwt. of ore.\* It is approved practice to accumulate stocks of pyrites convenient to each set of burners, for the purpose of enabling the ore to get thoroughly dry before being burnt.

**Charging the burners.** The burners are charged by means of a long-handle shovel (2.5 cwt. is the charge) in the following rotation for each single unit:—

Burner No.	Hour of Charging time.	Hour of Dropping time.	Hour of using Pricking Bar.
1	2 and 8	7 and 7	1, 5, 7, and 11
3	4 and 10	9 and 9	3, 7, 9, and 1
5	6 and 12	5 and 5	5, 9, 11, and 3
2	3 and 9	2 and 2	2, 6, 7, and 12
4	5 and 11	4 and 4	4, 8, 10, and 2
6	1 and 7	12 and 12	12, 4, 6, and 10

The bed of the ore in the lump burners is about 9 inches to 10 inches deep, spread evenly over the surface, and rests on the square grate bars previously described.

Any dust in the ore being charged is distributed as much as possible around the side of the burner; this assists in overcoming the tendency of air entering the burner to creep up the sides. Care must be taken to see that the front of the burner is carefully charged first.

**Use of the pricking bar.** One hour before and three hours after each charging, the fire is sliced by means of a pricking bar—a long rod having a single prong 7 inches long at the end. The prong is buried in the fire just inside the small raking door, and pushed slowly and steadily right to the back of the fire. The fire is sliced once along the partition wall, once in front of the raking door, and once towards the centre of the fire through both raking doors, thus making six slicings for one burner. This procedure cuts through any skin of slag, and so keeps the fire open.

**Dropping burnt ore.**—The burnt ore is withdrawn through the grate bars by turning them first in one direction and then in another, through about  $\frac{1}{2}$ th of a whole turn. A bar is missed every time in going from one side of the furnace to the other, the missed bar being dealt with on returning. This ensures that only the lower layer is withdrawn. Too much care cannot be taken in dropping, otherwise unburnt ore will escape, with the consequent loss of sulphur, as well as reducing the depth of the new charge in the burner, reducing the resistance, and upsetting conditions which are essential to proper working.

**Operation of Herreschoff burners.**—The pyrites "fines" issuing from the overhead charging hopper are fed to the top shelf of the burner



## MANNHEIM PROCESS

by an intermittent worm, capable of regulation. When the feed of the ore is properly adjusted, the colour of the burning ore on the shelves should be—top shelf, no fire, dull appearance; second shelf presents a distinctly red appearance; third shelf or hot shelf, is bright red with flames; fourth shelf should have a visible glow at night; the fifth, or bottom shelf, should appear quite dead and black. The Herreschoff lump burners are hand-fed, and operated similarly to those already described.

**Air drying towers.**—The air passing in series through the two drying towers is thoroughly dried by sulphuric acid of 75 to 80 per cent. strength flowing down the first tower, and acid of 95 per cent. strength down the second, or final, drying tower. There are two lead-lined timber reservoirs of about eight tons capacity, one for each tower, the acid being elevated to the top of the tower from the circulating reservoirs by two 1½ inch centrifugal Kynoch pumps, driven from one common shaft by a 4 h.p. motor. Each pump is regulated to elevate about six tons of acid per hour. The fan driving the air through the drying towers has its capacity controlled by a damper in the suction pipe, in order to regulate the pressure of air in the burners.

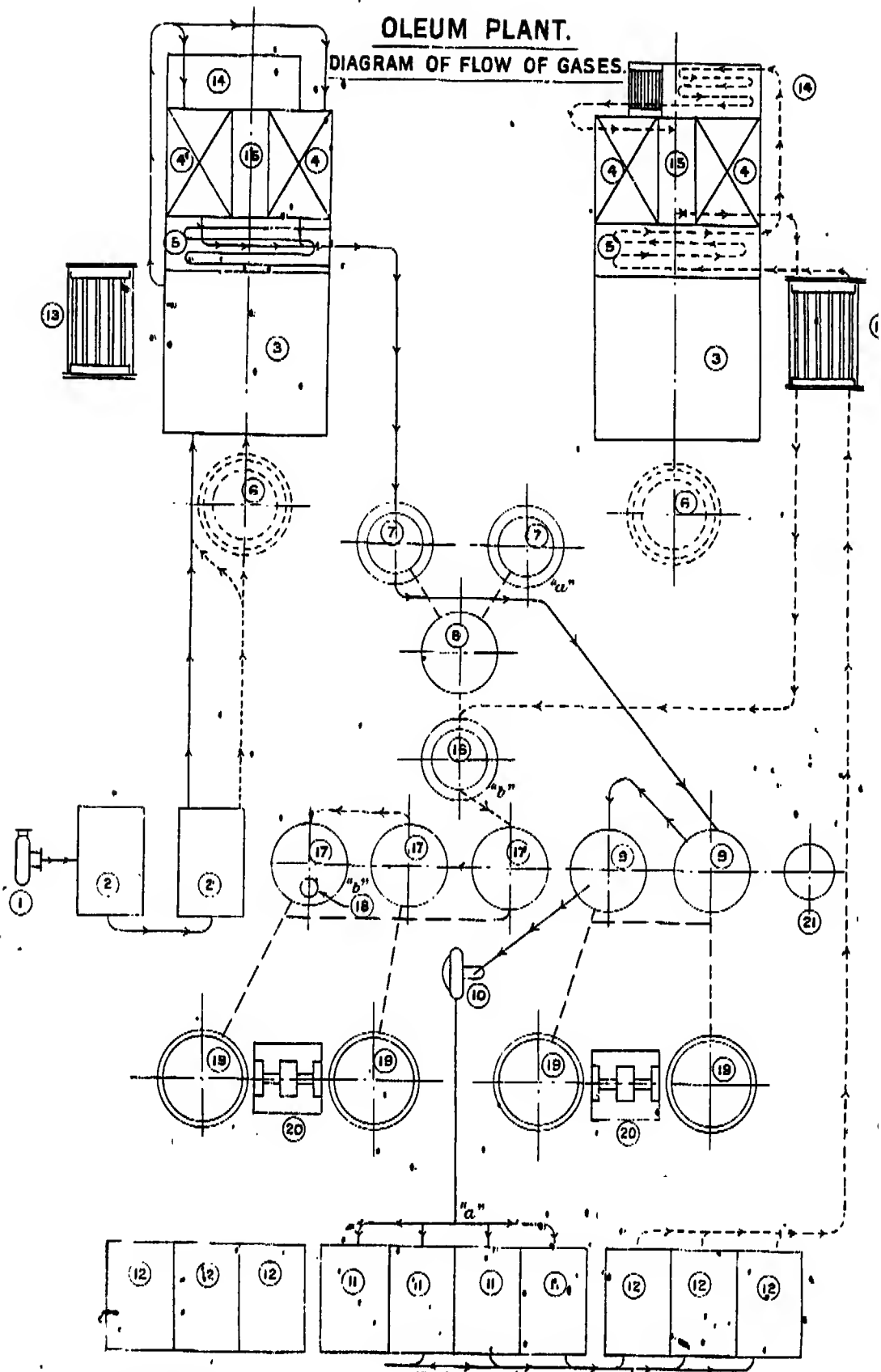
**Oxide shaft.**—It is essential in filling the oxide shaft to have iron oxide ore which has been screened to free it of all undersized ore below 1½ inches. It should be dry, and preferably fresh and warm from the burners, also well burnt. The depth of ore is adjusted to about 7 feet 6 inches, to give the best resistance in the shaft. Two inches of ore are dropped out every morning, and two inches of fresh ore charged in at the top.

**Superheater.**—The coke fire in the superheater must be regulated so that the temperature of the gases to be heated is raised to about 470° C. After the platinum mats have been in use for some time, it is necessary to raise this temperature to 480° C. or 490° C., to correct the poisoning actions of arsenical compounds which are liable to escape in the existing inadequate purification system.

**Platinum contact shaft.**—In time the mats get so poisoned with arsenical compounds that they must be taken out and replaced by fresh ones. The poisoned mats can be purified by washing in a dilute solution of hydrochloric acid. The rewashed mats are not as satisfactory as new ones, and can only be revived in this manner about twice, as the asbestos fibre mat tends to fall apart. By eliminating moisture in the air entering the burners, one of the carriers of arsenical compounds is removed. By attending regularly to the repacking and cleaning of the acid catchers and filters, acid mist, which is another source of carrier of catalyst poisons, can be trapped to some extent.

**Absorption system.**—The absorption is done in two stages: first, the absorption of the  $\text{SO}_3$  which has been converted in the oxide shaft, and secondly, the absorption of the remaining  $\text{SO}_3$  converted in the platinum contact shaft. The entire system, however, must be considered as one absorption unit.





**FIG. 5A**

Fresh feed acid is distributed over towers 2 and 5, these being the final towers of the two stages mentioned above. The acid from these towers runs back into receiver No. 1, and a portion is passed forward into receiver No. 2, being then pumped up into tower No. 1, returning into receiver No. 2, a portion being passed forward into receiver No. 3. From this receiver the acid is circulated over tower No. 4, returning into receiver No. 3, a portion being forwarded into receiver No. 4. The acid in this last receiver is pumped over tower No. 3, and run back into receiver No. 4. The acid gradually increases in strength by absorption of  $\text{SO}_3$  until finally, in receiver No. 4 it is in the form of oleum, with 20 per cent. free  $\text{SO}_3$ . For this reason arrangement is made for pumping the acid in No. 4 receiver direct to storage, in addition to being able to elevate it to tower No. 3.

The strength of acid in the receivers varies as below :

No. 1, 98 per cent.; No. 2, 5 per cent. free  $\text{SO}_3$ ; No. 3, 10 per cent. free  $\text{SO}_3$ ; No. 4, 20 per cent. free  $\text{SO}_3$ .

For the purpose of regulating these strengths, acid can be passed forward or backward to the receivers as desired; 95 per cent.  $\text{H}_2\text{SO}_4$  as feed acid is run into receiver No. 1, while 20 per cent. oleum is run to storage from receiver No. 4.

The path of the gases is as follows :—from oxide shaft, through coolers, to bottom of tower No. 1; from the top of No. 1 to bottom of No. 2; from top of No. 2 through system described, back from platinum shaft, through coolers, to bottom of tower No. 3; from No. 3 to bottom of No. 4; from No. 4 to bottom of No. 5; from top of No. 5 to exit into atmosphere.

For clearness, the whole course of the gas may now be traced again (Fig. 5a) :—

(1) Dry air enters the pyrites burners, being forced through the air drying towers by an air blower.

(2) The pyrites burns and gives off sulphur dioxide.

(3) The mixture of sulphur dioxide and air passes through the mass of burnt pyrites in the oxide shafts, where about 35 per cent. of the  $\text{SO}_2$  is converted to  $\text{SO}_3$ , and the larger proportion of arsenical compounds and other poisons are trapped.

(4) This  $\text{SO}_3$  with unconverted  $\text{SO}_2$  and air, leaves the oxide shaft.

(5) The gas mixture passes over the preheater pipes; gives up part of its heat to heat up the gas in these pipes, which is on its way to the superheater.

(6) The partly-cooled mixture is further cooled in water-cooling towers, and leaves for the absorption towers Nos. 1 and 2.

(7) The cooled gas passes through these absorption towers in series.

(8) The  $\text{SO}_3$  is taken out of the mixture.

(9)  $\text{SO}_2$  and air leave the second absorption tower, drawn by the fan.

(10) Gas forced by fan through purification system—that is, acid catchers and filter boxes. Any trace of  $\text{SO}_3$  or  $\text{H}_2\text{SO}_4$  mist is here trapped, runs from the bottom of the purifying system, and is pumped away from the plant, as it contains much arsenic.

(11) The purified gas passes through the inside of the tubes of the heat exchanger, where it is heated by hot gases from platinum shaft.

(12) It passes through the forewarmer pipes in the oxide shaft. Here it is further heated by the hot gases from oxide shafts passing over these pipes.

(13) It passes through the coke-fired superheater pipes, and the heating to proper temperature is completed.

(14) The hot mixture of  $\text{SO}_2$  and air passes through the platinum mats, where, with new mats and good conversion, 88 per cent. of the remaining  $\text{SO}_3$  is converted. This gives a total of 92 per cent. over-all conversion.

(15) Sulphur trioxide, a little unconverted sulphur dioxide, and air passes from the platinum chamber.

(16) These hot gases pass round the heat exchanger pipes, and are partly cooled by the cold gas passing through the heat exchanger pipes.

(17) Gas finally cooled in water-cooled tower.

(18)  $\text{SO}_3$  converted in the platinum shaft and a small amount of unconverted  $\text{SO}_2$  with air, enter the absorption towers 3, 4 and 5 in series, after which the remaining gas passes to the atmosphere.

#### PLANT CONTROL.

Samples of the gases are regularly taken and tested for percentage of  $\text{SO}_2$  in the burner gas, and with good working conditions this should average 6 per cent.  $\text{SO}_2$ .\*

Samples of burnt ore are daily tested for sulphur content, and should average not more than 3.5 per cent. of recoverable sulphur. There is, of course, always more or less sulphur existing as sulphates, depending on the class of ore, which is impossible to recover.

Samples of gas from the oxide shaft entering No. 1 absorption tower are regularly tested for percentage of  $\text{SO}_2$  which, with clean-burnt ore packing and good work, should indicate a conversion in the oxide shaft of 35 per cent. It is most important that the oxide shaft should do its allotted share of conversion, so as not to overload the platinum shaft.

Samples of gases from the inlet to the platinum shaft and inlet to No. 3 absorption tower are similarly tested for the purpose of determining the conversion in the platinum shaft. With new mats and good working, these tests should indicate a conversion of 88 per cent. in the platinum shaft; but, in practice, an average conversion of 80 per cent. is with difficulty maintained when there is arsenic in the

\* (See page 37.)

ore. Ore with over 0.1 per cent. of arsenic as  $\text{As}_2\text{O}_3$  is almost unworkable with the existing purification system. Pyrometers are fitted for ascertaining the temperature in the centre of the oxide shaft, also the temperature of the gases entering the platinum contact shaft. The temperature in oxide shaft in the centre of the mass varies from  $560^\circ\text{C}$ . to  $600^\circ\text{C}$ . A higher temperature would give better conversion, but is impossible to attain with the existing plant.

Manometers are fitted in various parts of the plant which give indication of irregularity of working through chokes of absorption towers, etc., by the formation of sulphate sludge.

#### SOME NOTES ON THE WORKING OF THE PLANT

From page 11 to 37 a more detailed account is given of the working of the plant and of experiments carried out in connection with it, as well as an attempt to construct a heat balance of the process.

**Burners.** —At first, owing to the inexperience of the men who were available for working the burners, it was difficult to get uniform results and keep the sulphur left in the burnt ore down to a minimum.

Trials were made of fires of depths from 10 to 20 inches. The 20 inch fires were found to be extremely sensitive, very readily cooling off or heating up too much with bad results in either case. Gradually, however, good results were obtained with both fires, as experience in working them was obtained, but the opinion is that in running a large plant where close individual supervision of the burners is not possible it would be more satisfactory to run with shallow beds, provided great care were exercised by the men in dropping the fires. The large number of separate lump burner fires which demand attention if the best results are to be obtained make it desirable to have as many Herreschoff burners as possible as these require much less supervision and labour.

#### *Report on special method of working pyrites burners at H.M. Factory, Queen's Ferry.*

One section has undergone an experimental run with the object of finding out:—

(1) The depth of fire required which would be easily workable and which would give consistently low sulphur content in the burnt ore.

(2) The method of treating the fire in order to prevent the formation of "clinkers."

(3) The charges which fires of various depths would take, so as to allow them to be thoroughly burnt, three hours after charging.

(4) The best method of raking and shaking for a hand-charged pyrites fire.

(5) The ideal condition of the burners, consistent with the maximum efficiency of the plant.

With these objects in view, the fires on No. 1 unit were lowered to a depth of 10 inches, and the fires on No. 2 unit raised to 16 inches.

The 10 inch fires were originally given a charge every six hours, raked three and five hours after charging, and dropped an hour before each charge. In order to systematise the work on all the fires, it was necessary that a definite weight of pyrites should be put on the fires at charging time. It was found that two 12 shovel charges, as given by two burnermen differed in weight by 0.25 cwt., a difference which would show itself three hours after charging when the fires would not be ready for raking, and consequently not ready for charging after six hours. It is absolutely necessary that each fire should be charged, raked, and shaken at the hour prescribed for it. This can only be attained by getting the fires into good condition, and then giving to each fire the charge which will be burnt out in six hours.

Boxes were made which would just contain a half charge of pyrites. These boxes were required to be 12 inches by 17 inches by  $8\frac{1}{2}$  inches, and the burnerman must fill this box twice in order to get the proper charge. This charging of a definite weight of pyrites soon brought the fires into that steady state which is so essential to good burning. The results of this good burning may be seen from the graph (Fig. 6). With charges given by a certain number of shovels and not by a definite weight, the sulphur content of the burnt ore varied considerably, but after a month's run with definite charges by weight, steady results of between 1.7 per cent. and 2.2 per cent. were obtained. This increased burning of the pyrites showed itself in the increased efficiency of the plant, which is kept between 88.0 per cent. and 91.0 per cent.

*Method of raking.* The rakes employed were of  $1\frac{1}{4}$  inch steel, and had one prong 6 inches long; this prong was chiselled at its front and back edges, and was pointed at its end. In all raking that is properly done it is absolutely necessary that the whole prong of the rake be embedded in the ore, by this means, a 6 inch depth of ore is disturbed and all dust is thrown down to the bottom of the fire from which it is removed by shaking.

The most satisfactory method of raking is the one as shown in diagram (Fig. 7). Clinkers will always form where dust collects and the fires are hot enough; it is therefore necessary to remove all dust from back and sides of furnace, *i.e.*, the places where most dust collects. The burner-man commences his raking by making the prong of the rake sink in its full 6 inches into the ore at the back of the fire right up against the wall. The rake is then drawn towards the front of the furnace, keeping the prong well embedded until the middle of the fire is reached, when the rake is removed and dropped into the ore again by the wall at the back, and once more drawn to the middle of the fire.

When the whole of the wall at the back and sides has been cleared of dust, the fire is raked in the same way from the front to the middle, the rake itself being pushed in this case instead of being pulled.

In order to make certain that no dust remains, it is advisable to re-make the fire, as shown in diagram, for a distance of about 6 inches from the back and sides all round. A two-pronged rake is now used to level the pre, and the fire is ready for dropping.

# • MANNHEIM PLANT PERCENTAGE OF SULPHUR IN BURNT-ORE.

• Fires with Shallow Beds. (10")  
 — " " " Deep " (20")

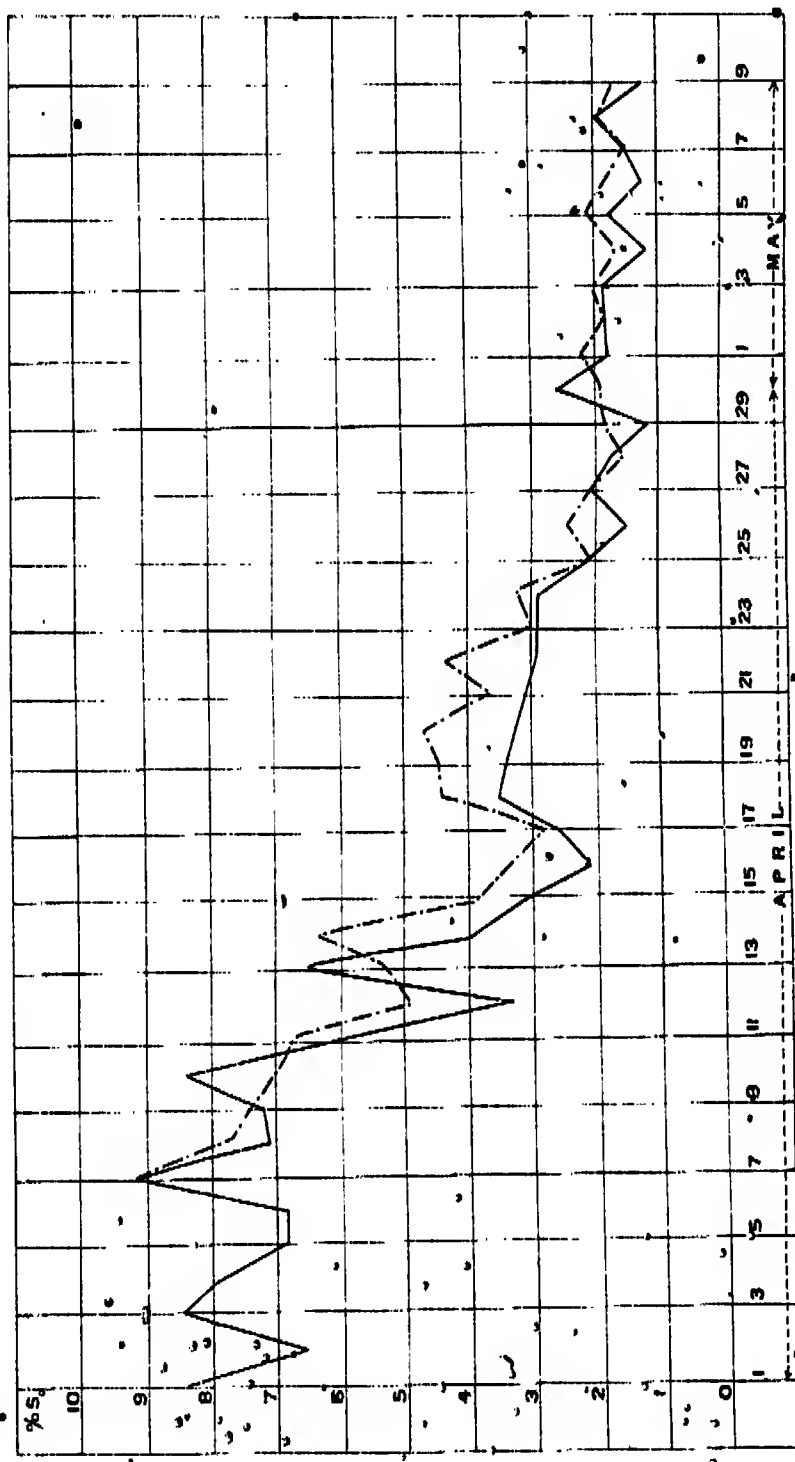
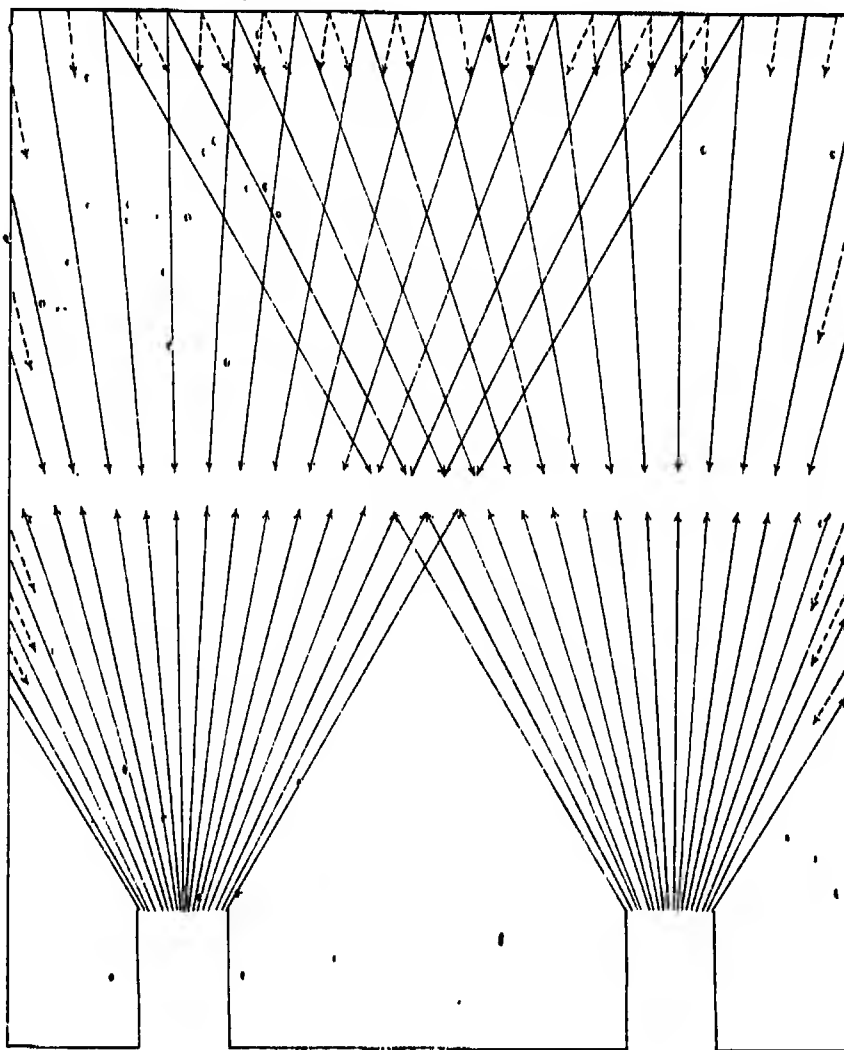


FIG. 6.









**METHOD OF RAKING A PYRITES FIRE**  
**AS ADOPTED AT H. M. FACTORY, QUEEN'S FERRY.**

*Three Stages.*

- I. Pull rake from back and sides to centre of fire.*
- II. Push rake from raking doors to centre of fire.*
- III. Re-rake bed of furnace from walls at back and sides.*

**FIG. 7.**

*Dropping.*—This operation is one that requires considerable care and is, perhaps, the most important which a burnerman has to perform. A good fire may be entirely spoiled by under or over dropping. The key is put on the bars, and is quickly turned four or five times through an angle of about  $45^{\circ}$ . This is sufficient to shake all dust into the hopper and leave the large pieces still in the fire. Mistakes have been made before in allowing burner men to twist the handle of the key through  $360^{\circ}$  time after time. This method not only removes dust, but also lumps and half-burnt pyrites are forced between the bars into the hopper below, and over-dropping results.

*Times of charging.*—All fires previously had been timed for charges, rakings, and droppings at the hour. As a systematic method of running the burners was desired, it was necessary to time each operation so that at any moment it was possible to tell exactly what was being done on the burners. The scheme adopted was as follows :—

Ten minutes before each hour - Fires to be raked which have burned approximately 3 hours after their charge.

At the hour - - - - - Fires to be charged.

Ten minutes after each hour - Fires to be raked and dropped which have burned approximately 5 hours after their charge.

This system allows 2 hours 50 minutes for the  $2\frac{1}{2}$  cwt. charge to burn off before the first raking, and 5 hours 10 minutes between charging and dropping. These times have worked exceedingly well since the fires have been charged with a definite weight of ore.

*Formation of clinker.*—Previous experience in the management of pyrites fires led to the belief that at times the formation of clinker was unavoidable. Over a long period on one section it has been proved that with efficient raking, shaking and charging, and with whatever depth of fire, clinkers need never form. With the 10 inch fires, using a 6 inch pronged rake, the fires can be kept perfectly clean over any length of time and give no trouble at all. With the 20 inch fires, which are far more sensitive than the low fires, it is just as easy to prevent any hard clinker, but on several occasions soft clinker has been found, which has been easily broken up, in the fire; so long as fires are kept free from clinker, especially the deep fires, it is unnecessary to poke them. All poking of fires at Queen's Ferry was strictly forbidden. With the deep fires, where each successive charge forms a layer on the top of the previous charge, it is absolutely necessary to see that these layers are not mixed. If the fires are hot and clean a charge is burnt out thoroughly before the next charge is put on. This burnt charge gradually finds its way down to the bars, cooling as it descends with each shaking, until at the bottom of the fire it is just warm and ready for dropping into the hopper. If any poking is allowed on these deep fires it will mix the layers of ore in various stages of burning, and by throwing deep down into the fire some of the partially burnt will assist in the formation

of new clinker. Once this disturbance has taken place clinkering will inevitably follow until the bed of ore once more takes up its original state in layers.

The deep fires containing as they do a very dusty layer on the bars at least 6 inches deep, must be shaken at the proper time very carefully: any overcropping will result in a space being left between the bars and the bottom of the fire, which will persist until the fire is next charged, when the weight of the fresh ore put on will cause the bed to sink and lower the thickness of the bed considerably.

Analysis of the burnt ore from the 10 inch fires at the beginning of the experimental run showed that from 5 per cent. to 8 per cent. sulphur remained in the ore. But as the burner-men were unused to the new method of handling the fires, this was only to be expected. As soon as they had settled down into the systematic running of the fires, these results at once began to fall, and for the last fortnight the unburnt sulphur in the ore varied from 2.2 per cent. to 1.6 per cent.

With the deep fires the sulphur content gradually fell in the first fortnight, but in a much more gradual manner from 8 per cent. to 3 per cent., and during the last fortnight averaged 2.1 per cent. sulphur.

During the latter part of the run, the sulphur content of the ore from the two sets of fires differed only slightly from one another, but in almost every case the ore from the deep fires contained a slightly higher percentage of sulphur than from the others.

A series of tests was run on beds of various thicknesses, and it was found that for a deep fire, when the top of the bed was on a level with the bottom of the charging door, the fire began to cool and remained rather cooler than was required. The best depth in order to get good burning throughout and maintain the requisite amount of heat in the fire, was to keep the top of the fire about 4 inches below the lower level of the charging door. With this depth it is possible to maintain good fires free from clinker and burnt ore of low sulphur content.

A graph of the amount of sulphur in the burnt ore from the two sets of fires is given (Fig. 6).

In making a comparison between any two sets of fires, it is necessary to take into account ease of working with all the other factors. Judging from this standpoint, the 10 inch fires have easily proved themselves to be better than the deep ones for the following reasons :—

- (1) They are easier to work.
- (2) The burnt ore from 10 inch fires contains slightly less sulphur than the others.
- (3) Complete absence of clinker either hard or soft.
- (4) They can be worked by men who are not experienced burner-men.
- (5) Any mistake in over or under dropping by any burner-men can be more quickly remedied in low fires than in deep ones.

During this period the efficiency rose to 92 per cent. on two occasions and averaged 89 per cent., the extra efficiency being accounted for by

the increased burning of the pyrites with the resultant lowering of sulphur content of burnt ore.

Using this method of treating pyrites burners as described in this report, it has been proved that the Mannheim plant can be run continuously at an efficiency of 88 per cent., with burnt ore never giving a figure higher than 2.5 per cent. of sulphur, each section producing 1.2 tons  $\text{SO}_3$  per day.

**Air drying.**—The air supplied to the burners for the combustion of the pyrites is forced by means of a Sturtevant fan through two lead drying towers in series which serve two units. Sulphuric acid (94 per cent.) is circulated over these towers by means of a centrifugal pump. The circulating acid is kept at 94 per cent. by a constant inflow of 98 per cent. acid and a constant outflow of 94 per cent., the latter being used as feed for the unit. The efficiency of this air-drying system is 95.96 per cent., the moisture in the air entering the burners never exceeding 0.3 grams. per cubic metre. As a result of this the acid in the settling tanks from the coolers is very small in quantity and high in strength, that from the oxide coolers containing on the average 10.12 per cent. free  $\text{SO}_3$ , and that from the platinum cooler 22.24 per cent. free  $\text{SO}_3$ , the amount collected from the oxide coolers is about 0.06 ton per 24 hours per double unit | 0.062 ton per 14 days from the platinum coolers.

Further, the amount of sludge settled in the bases of the coolers is almost negligible after five months running.

Originally the acid was raised to the top of the drying towers by Kestner elevators, and then the drying was much less efficient and erratic than after centrifugal circulating pumps were employed, which enable a much larger quantity of acid to be passed over the towers.

The object of drying the air supplied for combustion of the pyrites is two-fold: (1) to avoid production of weak acid by combination of the moisture with the  $\text{SO}_3$  formed in the oxide shaft, which would corrode the steel cooler, and give rise to arsenicuretted hydrogen; and (2) because moisture in the gases helps to carry forward any arsenic which may be present.

**Oxide shafts.**—To maintain the shafts free and in a workable condition about 150 lb. of oxide are dropped from each shaft per day, and this is replaced by an equal weight of fresh screened lumps (held by  $1\frac{1}{2}$  inch mesh) from the lump burners. Experiments showed that dropping of oxide from shafts militated against a high efficiency for some hours, and it would appear that a daily dropping is inadvisable, provided the shafts are free and do not offer too high a resistance to passage of the gases and that the arsenic content is not excessive.

**Cooling towers - Oxide coolers.**—It was found advantageous to alter the original arrangement of the acid outlets at the bottom of the cooler by butting them into a sludge tank so designed that the pipes could be easily cleaned without disconnecting them. All acid from cooling towers settling tanks along with drins from the main fan filters and

acid catchers, was led into special tanks and pumped away from time to time for use in the nitric acid retorts, as it contained arsenic.

**Purification of gas.**—Gases leaving the second absorption tower are wet with acid and must be purified before being admitted to the platinum shaft.

The extent of purification required depends mainly on two factors :—

(a) The amount of moisture entering the system—this with  $\text{SO}_3$  produced in the oxide shaft forms sulphuric acid, part of which exists as mist, and in this finely divided state is very difficult to eliminate.

(b) The quantity of acid flowing down the second absorption tower.

The table below shows that the quantity of acid condensed by the main fan in No. 9 section, where a very large flow of acid was possible, is very large compared with the amount condensed by the main fan in other units with normal flow. The strength of acid condensed by the fan is invariably the same as that circulating in No. 2 tower, which shows that this acid is carried over by fan suction.

The purification is effected by means of—

(a) Main fan, the centrifugal action of which eliminates about 75 per cent. of the total acid carried over by suction as described above.

(b) Four quartz packed acid catchers through which the gases pass in parallel. These remove the greater part of the remaining acid.

(c) Six filters packed with a layer of quartz at bottom, on which rests the main filling of blast furnace gravel basic slag, followed by a layer of asbestos in which is incorporated a little lime and magnesia. These should condense any acid passing the acid catchers. In practice, however, a small amount varying from 7-130 milligrams per cubic metre fails to be trapped, and as this is presumably formed in oxide shafts and burners it will undoubtedly carry arsenic forward to the platinum shaft.

*Acid dripping from fan per day.*

Section.							
1	3	4	5	6	7	8	9
Cwt. 3.1	Cwt. 3.85	Cwt. 3.1	Cwt. 4.75	Cwt. 5.36	Cwt. 4.2	Cwt. 3.1	Cwt. 11.4

*Acid dripping from catchers and filters per day.**Section.*

5	6	7 and 8	8 and 10
Cwt. 1.8	Cwt. 1.86	Cwt. 3.2	Cwt. 3.75

The following table gives the amount of acid "mist" calculated as grams of  $H_2SO_4$  per cubic metre, entering the platinum shaft on five different dates:—

*Section.*

1	2	3	4	5	6	7	8	9	10
1 —	—	—	—	—	0.014	0.129	—	—	0.068
2 —	—	—	—	—	—	—	—	—	—
1 0.012	0.033	0.009	0.014	0.018	0.014	0.030	0.71	0.017	0.068
2 0.045	0.028	0.010	0.016	0.015	0.004	0.129	—	0.020	0.007
1 —	—	—	—	0.17	0.018	0.025	—	—	0.010
2 —	—	—	—	—	0.012	0.047	—	—	0.026
1 0.003	0.003	0.012	—	—	—	—	—	—	—
2 —	—	—	—	—	—	—	—	—	—
1 —	—	—	—	—	—	—	—	0.024	0.027
2 —	—	—	—	—	—	—	—	0.026	0.028

It is seen that the results are variable, showing that some of the acid catchers were not capable of dealing with the amount of mist satisfactorily. One return after five months running showed 0.095 gram. per cubic metre of mist in the gases leaving the filters for the heat exchangers. The gases entering the acid catchers contained 1.62 grams. per cubic metre, so that the efficiency of the filtering system is 94.1 per cent. But this is not good enough, and the filtering system is not equal to the demands laid upon it.

The quantities and strengths of acids from this section were as follows:—

Source.	Strength calculated as $H_2SO_4$ .	Quantity collected per 24 hours.	Arsenic content in parts per million.
	Per cent.	Lb.	
Oxide coolers	101.3	134	600
Platinum coolers	195.1	10	45
Main fan	99.1	28	180
Acid catchers	95.9	156	—
Filters	—	nil	—



Gas passing through filters and catchers (1 section) per 24 hours  
 = 1,140,300 cubic feet.

= 32,300 cubic metres.

Mist removed per cubic metre 1.525 grams.

∴ Mist removed per 24 hours =  $\frac{32,300 \times 1.525}{453.6}$   
 = 109 lb.

**Absorption of  $\text{SO}_3$ .**—The absorption system is well up to the work required of it. Given a constant feed of 94 per cent. acid and the plant run to produce 20 per cent. oleum, the handling of the system is comparatively easy, and an efficiency of practically 100 per cent. can be obtained.

The acid circulating in Nos. 2 and 5 towers must in all cases be maintained at a strength of 98 per cent.

The principal factors in determining the efficiency of the absorbing system are: (1) temperature, and (2) concentration of the absorbing acid. The temperature factor depends to a large extent on the temperature of the gases leaving the oxide and platinum shafts and on the efficiency of the cooling system, which, in its turn, depends most largely on the water supply.

The average of a number of temperature determinations in the four acid reservoirs is as follows:—

*Reservoir.*

1.	2.	3.	4.
53° C.	64° C.	58° C.	61° C.

The absorption is accompanied by evolution of heat the hottest reservoir being the one receiving acid from the towers normally showing most absorption.

The following temperatures of gases entering the towers were taken:—

Section.	Entering absorption towers.					Exit.
	1	2	3	4	5	
2	90°	55°	50°	38°	35°	40°
8	48°	42°	57°	43°	36°	41°
3	60°	43°	76°	40°	32°	38°
6	56°	46°	69°	43°	39°	46°

In the case of section 2 there were only two oxide coolers, which accounts for the high temperatures of the gases entering towers 1 and 2. It will be seen that the gases leaving tower 5 are hotter than those entering on account of the evolution of heat during absorption above referred to.

**Main fans.**—The glands of these fans should be packed with white asbestos dipped in flake graphite, not less than once in eight weeks. It would have been far better if the stuffing boxes had been made much deeper, as they do not hold two rounds of packing properly, and as the centres of the spindle bearings are as far apart as 4 feet 3 inches, the packing gets hard, causing the fan to vibrate badly.

**Superheater.**—Superheater pipes have been the cause of a great deal of trouble. The pipes are badly designed. There are not sufficient bolts in the flanges (six only), and instead of holes in the flanges there are slots with a raised face inside the bolt circles. These slots are also in the wrong places.

It does not seem reasonable to provide a 12 inch pipe with 12 holes, not slots, when it is subjected practically to no strain and is out in the open and easily accessible, while a 10 inch pipe buried in brickwork and subjected to severe heat should be provided with only six slots.

It was also found that the ends of the vertical pipe were not always in the same place, in one case there was as much as  $\frac{1}{4}$  inch difference, thus making it still more difficult to make a good joint between a "U" bend and these two pipes.

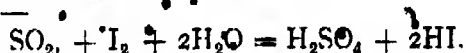
**Gas testing.**—The gas analyses consist principally in the estimation of  $\text{SO}_2$  and oxygen. The oxygen is determined by absorption in alkaline pyrogallol, or phosphorus in an Orsat apparatus,  $\text{SO}_2$  is estimated by absorption in standard iodine solution or caustic soda solution. Attempts were made, at one time, to estimate both  $\text{SO}_2$  and oxygen in the Orsat apparatus, using strong iodine solution for the  $\text{SO}_2$  and pyrogallol for the oxygen; but, owing to the fact that the gas was collected over water, erratic figures were obtained for the  $\text{SO}_2$  determinations. A certain amount of the  $\text{SO}_2$  was taken up by the water, so that the final amount 100 cc. of gas collected for analysis, was poorer in  $\text{SO}_2$  and correspondingly richer in oxygen.

Reich tests taken simultaneously with those in the Orsat always gave higher results, and these again were confirmed by an analysis in another Orsat apparatus, but collecting over mercury.

$\text{SO}_2$  then cannot be estimated by absorption in iodine in the Orsat apparatus. Paraffin in collecting tube of Orsat was also tried.

Two other methods of estimating  $\text{SO}_2$  have been employed with success: (1) The Reich test, where the gas is drawn through a known volume of standard iodine by means of a syphon, the amount of water syphoning over being measured in a graduated cylinder. In the first method, the gas is aspirated through the starch iodine solution, until the blue colour is just discharged, or until a certain depth of blue is reached. The volume of water syphoning over is equal to the total volume of gas less the  $\text{SO}_2$  absorbed.

The equation—



shows that 254 gm.  $\text{I}_2$  absorb 64 gm. of  $\text{SO}_2$ , i.e., 22.4 litres of  $\text{SO}_2$  at  $27^\circ\text{C}$ .

NTP or 0.127 gm.  $I_2$  (1 c.c. of N iodine) absorb 11.2 c.c. of  $SO_2$  at NTP. It is not possible, working the test in the ordinary way to obtain results correct to the second place of decimals. For example, suppose in a test 10 c.c. of N/10 iodine are used, and collect 500 c.c. of water, as the volume; then, with varying temperature of the gas results will be obtained varying in the second place—or even the first place.

Thus, calculated to 0° C.—

$$SO_2 = 2.24 \text{ per cent.}$$

Calculated to 10° C.—

$$SO_2 = 2.32 \text{ per cent.}$$

Calculated to 20° C.—

$$SO_2 = 2.40 \text{ per cent.}$$

As no temperature corrections are made, it will be seen that figures in the second place of decimals are meaningless. The error in reading the volume of water, is generally 5 c.c., and one volume lower than 500 cc. this error will manifest itself, making the figures even more inaccurate. With careful working, however, determinations correct to the first place can always be obtained.

The value of any single test either for  $SO_2$  or oxygen depends upon the purpose for which the data are required.

It has been shown that the composition of the gas in various parts of the gas circuit, depends *inter alia* upon the time and method of charging the burners, and the activities of the two catalysts, it is obviously unsafe, therefore, to draw any general conclusions from the results of analysis of any one sample of gas, unless the sample of gas has been drawn continuously over a period of at least one hour.

It has been found that the variations in the gas compositions recur hourly under normal conditions, so that the data will depend upon the time they are taken.

This is clearly shown by the results obtained when "snap" tests were employed; morning and evening tests invariably gave divergent results, and in spite of calculated conversions of 90 per cent. and over, the plant did not turn out the amount required by this figure.

(2) For data upon which statistics, efficiencies, &c., have to be founded, it is obvious that snap tests cannot be relied upon; a constant and continuous sample of gas must be drawn and analysed so that all fluctuations and variations in the working of the unit, are represented in the final result. For this purpose the gas is slowly aspirated through an absorption bottle containing a known volume of standard caustic soda, and some hydrogen peroxide; all acid gases ( $SO_2$  and  $SO_3$ ) are absorbed in this, the resulting sulphite being oxidised to sulphate by the peroxide; the residual gas (oxygen and nitrogen) passes over into the aspirator, which is graduated and provided with a gauge glass; the test can thus be allowed to run for a considerable time—usually 20-24 hours—the contents of the bottle are then titrated with standard  $H_2SO_4$  with methyl orange as indicator, an excess of alkali must always be present to ensure that only normal salts are formed.

The oxygen is estimated in the residual gas in the aspirator, using an Orsat apparatus; by this method a total acidity figure is obtained, but it has been shown that in normal working, the escape of  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  mist is so small as to be negligible, and the result can be calculated as  $\text{SO}_2$ ; in cases of bad absorption, the test is stopped until normal conditions again obtain. The occasions on which this measure has had to be resorted to being very rare.

*Composition of burner gases.* Attempts to analyse the gases direct from the burners by the methods used for the exit gases, *i.e.*, by estimating the  $\text{SO}_2$  in iodine or caustic soda either in an Orsat or by the Reich method, led to failure, very low results being obtained in every case.

The difficulties of the estimation are obvious; there are no facilities for obtaining a composite sample from all the burners; a sample can be taken from every three burners and two of these can be combined, so that two separate and simultaneous determinations must be performed for each unit. The temperature of the gas may be anything from  $600^\circ\text{C}$ . to  $800^\circ\text{C}$ ., or even higher, and whatever gas equilibrium between  $\text{SO}_2$  and  $\text{SO}_3$  there may be, will be disturbed, so that ordinary estimations of these gases will not yield dependable results. No useful purpose can be served therefore, by attempting to get reliable burner gas figures from a determination by the Reich method, or in an Orsat apparatus. A continuous test using caustic soda, and aspirating the gas very slowly, did, however, yield reasonable figures. A table (I) is appended showing the burner gas figures obtained in a number of these experiments, and for comparison, the figures calculated from the exit gases over the same period. The formula used for calculating the burner gas from the exit gas analysis is

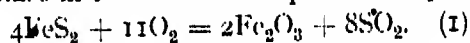
$$\text{SO}_2 \text{ per cent.} = 100 \times \frac{2}{3} \left( \frac{16,800 + 1.18a - 800b}{95,800 - 1,037a - 800b} \right)$$

where  $a$  = percentage  $\text{SO}_2$  and  $b$  = percentage  $\text{O}_2$  in the exit gases.

A series of determinations every few minutes over a period of an hour, using the Reich method were also made, tests on the exit gases being performed simultaneously. These figures are given in Table II., and show that, having regard to the experimental difficulties, the agreement between the calculated and experimental figures is quite close.

In all the experimental work, conversions and efficiencies have always been derived by calculation.\*

Certain of the formulae were worked out on the assumption that the reaction taking place in the burners is represented by the equation—



It is known, however, that the stoichiometric relations given by this equation do not hold exactly in the burners. Reliable data for the state of combination of the residual sulphur in the burnt ore is lacking, but there is every reason to believe that in a well-burnt ore, most of the sulphur is present as ferrous sulphide,  $\text{FeS}$ , with a small

\* See special description of method of calculation, p. 37.

proportion as  $\text{Fe}_2(\text{SO}_4)_3$ . A typical analysis is given in "Lunge," p. 446, showing 8.5 per cent. of the burnt ore as  $\text{FeS} = 3.1$  per cent. of sulphur.

*Table I.*  
*Experimental and derived burner gases.*

Time of expt.						Per cent. $\text{SO}_2$ in Burner Gas.	
						Found by expt.	Calculated from exit gases.
17 hours	-	-	-	-	-	5.3	5.6
17 "	-	-	-	-	-	5.4	5.6
17 "	-	-	-	-	-	4.9	5.5
17 "	-	-	-	-	-	5.9	5.6
17 "	-	-	-	-	-	6.2	5.7
17 "	-	-	-	-	-	4.6	5.2
17 "	-	-	-	-	-	5.3	5.5
17 "	-	-	-	-	-	6.1	5.9
17 "	-	-	-	-	-	5.0	5.5
17 "	-	-	-	-	-	6.0	5.7
20 "	-	-	-	-	-	6.4	5.9
24 "	-	-	-	-	-	5.5	5.5
24 "	-	-	-	-	-	5.4	5.5

*Table II.*

No.	Time.	Exit gas from oxide shaft.		Exit gas from platinum shaft.		Burner Gases.		
		$\text{SO}_2$ per cent.	$\text{O}_2$ per cent.	$\text{SO}_2$ per cent.	$\text{O}_2$ per cent.	Calculated from oxide exit.	Calculated from platinum exit.	Found.
1	11.40 a.m.	3.4	12.8	2.3	11.2	5.8	6.4	6.1
2	11.50	3.6	13.0	2.3	11.0	5.7	6.6	6.1
3	12.0 mld.	3.8	12.0	2.3	11.2	6.3	6.4	6.7
4	12.10	3.6	12.0	2.3	10.4	6.3	7.0	6.6
5	12.20	4.1	12.2	2.3	10.8	6.2	6.4	6.5
6	12.30	3.8	12.4	2.1	11.4	6.1	6.3	6.1
7	12.40	3.7	12.6	2.0	11.6	6.0	6.1	5.5
8	12.50	3.4				Av. = 6.1	Av. = 6.5	Av. = 6.2

The average burner gas from both calculations is 6.3, and the average of that found as a result of the series of single tests, is 6.2, showing that a good result can be obtained by averaging the figures from a series of snap tests.

temperatures showed minimum values at charging time, and maximum about an hour afterwards, corresponding with the maximum obtained in the case of burner gases.

**The pressure system.**—The pressure of the gas in the different parts of the circuit gives an indication of the resistances offered to the passage of the gas. The ordinary glass manometer has been employed in every

MANHEIM OLEUM PLANT.

Section IX, No. 1, Burner, 5.5.17

CURVE SHOWING VARIATION OF TEMPERATURE IN HERRESCHOFF - LUMP BURNER.

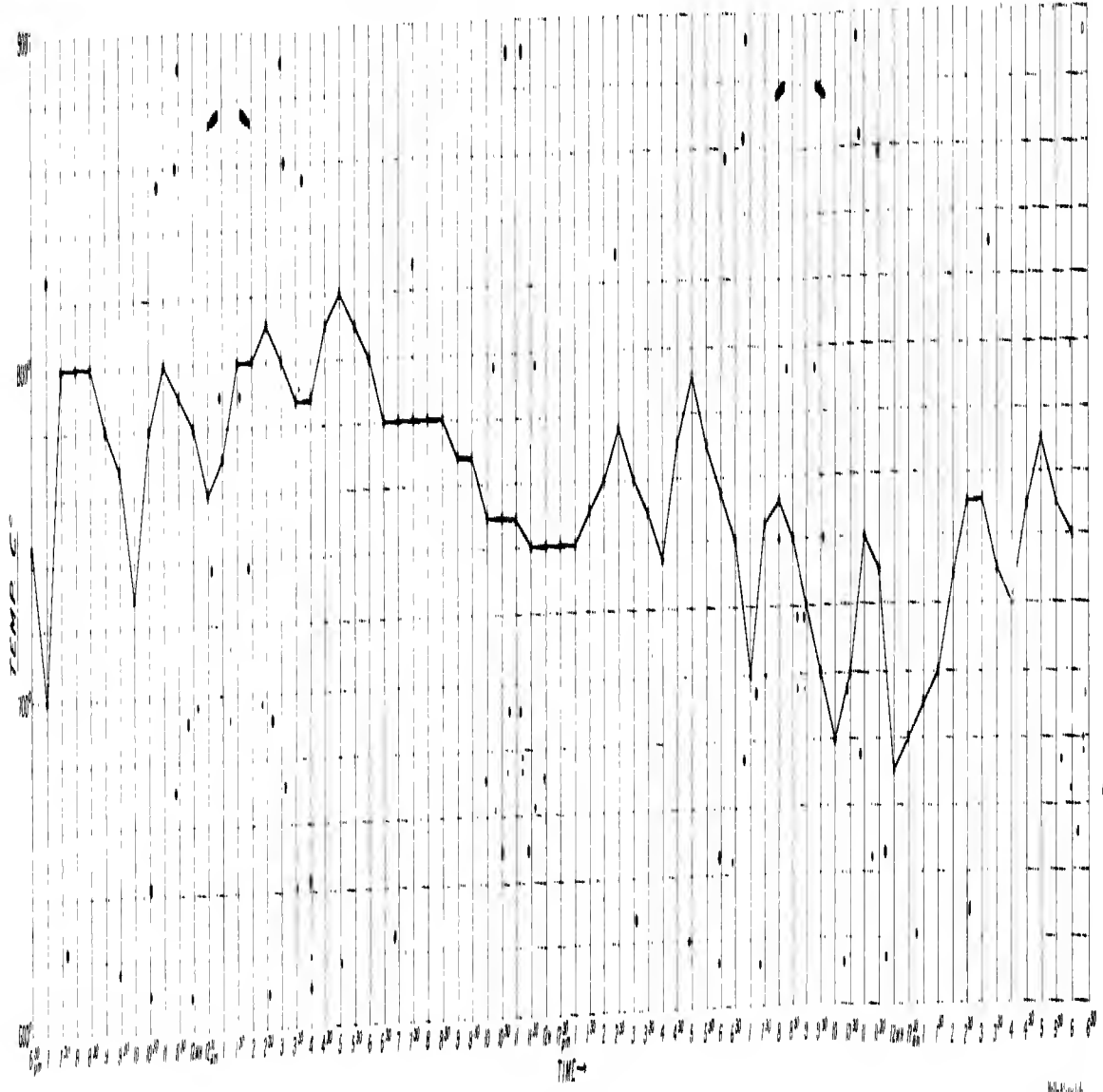


FIG. 7A

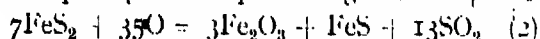
Assuming then, that the burnt ore contains 5 per cent. of sulphur, as FeS, and that the burnt ore is 70 per cent. of the original green ore, which contains 47 per cent. of sulphur, then—

- 5 parts of sulphur in burnt ore is 3.5 per cent. of the original ore, i.e. of the 47 parts of sulphur in the green ore, 3.5 eventually remain as FeS.

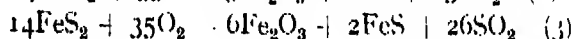
3.5 parts of sulphur = 9.6 parts FeS.

- Original ore contains 88 parts of FeS<sub>2</sub> (assuming all sulphur present as FeS<sub>2</sub>): therefore, 88 parts FeS<sub>2</sub> burn, yielding 9.5 parts FeS which is produced from 13 parts of FeS<sub>2</sub>, the remaining 75 parts of FeS<sub>2</sub> burning to Fe<sub>2</sub>O<sub>3</sub>; so that we have, 88 parts of FeS<sub>2</sub> producing 50 parts of Fe<sub>2</sub>O<sub>3</sub>, 9.5 parts FeS and 87 parts SO<sub>2</sub>.

The nearest simple equation representing this reaction is—

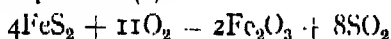


or



The value of  $r^*$  in formula (3) is in this case  $\frac{35}{26} = 1.346$ .

Whereas for the equation (1)—



it is 1.375.

With values of  $a^*$  under 3.0 the error caused by using the value 1.375 is not appreciable, but for values over this, the error exceeds 1 per cent. The conversion tables are calculated with value 1.375.

It has been found that the maximum efficiencies, consistent with commercial production, are produced with a burner gas of about 5.5 per cent.; the efficiency of the oxide catalyst depends primarily upon its concentration and temperature; the only means of altering its concentration is to alter the composition of the burner gas with respect to SO<sub>2</sub>. With a high burner gas, the concentration of catalyst is lowered. This can, of course, be controlled; but the question of burner gas temperature is not so easily disposed of, and as the burner gas temperature determines the temperature of the oxide shaft, it is a disadvantage having no pyrometer fittings in the oxide shafts. There can be no question that with the present system of charging not only does the composition of the burner gas undergo wide fluctuations but these fluctuations accompany the temperatures of the gases entering the oxide shafts. High temperatures are often reached in this way. Fig. 7A shows the temperature variations for a Herreschoff. The burner was charged with three shovels every three hours. The mean temperature was well over 750°. Except in two cases (7 a.m. and 10 a.m.), the temperatures showed minimum values at charging time, and maximum about an hour afterwards, corresponding with the maximum obtained in the case of burner gases.

**The pressure system.**—The pressure of the gas in the different parts of the circuit gives an indication of the resistances offered to the passage of the gas. The ordinary glass manometer has been employed in every



case, and cobalt nitrate solution has been found the most satisfactory liquid for filling the manometers, as it resists the action of  $\text{SO}_2$  and retains its deep pink colour for a considerable time.

In the following table is given the reading for each manometer, being the average of the readings taken every two days :

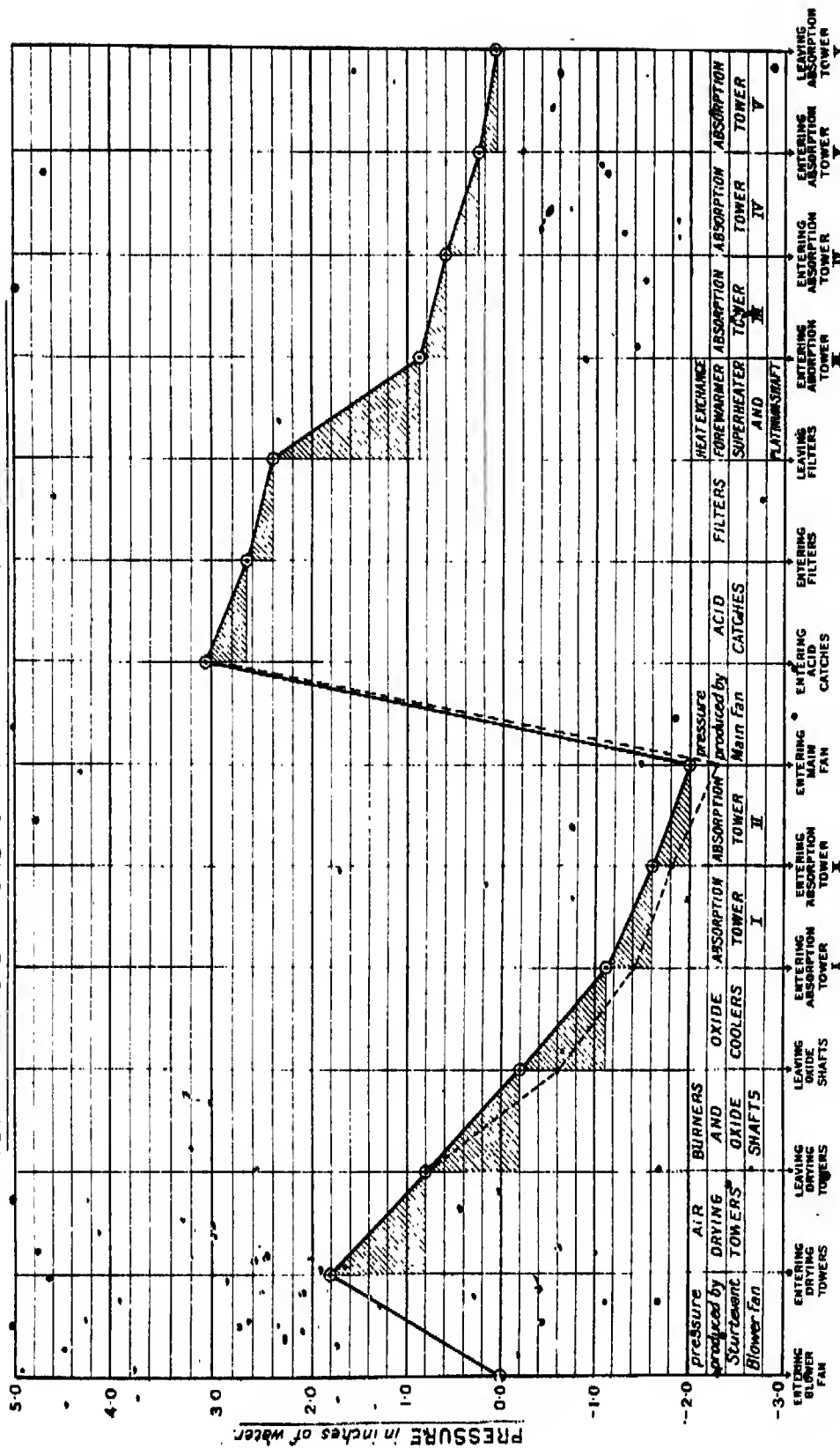
Location.	Section.			
	Lump.		Hereschoff.	
	Pressure.	Suction.	Pressure.	Suction.
To air drying tower - - -	1.8	-	1.8	-
From " " " - - -	0.8	-	0.8	-
" oxide shaft - - -	-	0.2	-	0.6
To abs. tower I. - - -	-	1.1	-	1.4
" " " II. - - -	-	1.6	-	1.8
" main fan - - -	-	2.0	-	2.3
" acid catches - - -	3.1	-	3.1	-
" filters - - -	2.7	-	2.7	-
Leaving filters - - -	2.2	-	2.2	-
To abs. tower III. - - -	0.9	-	0.9	-
" " " IV. - - -	0.6	-	0.6	-
" " " V. - - -	0.3	-	0.3	-

These points have been plotted on a graph (Fig. 8), where the difference between two consecutive manometer readings is taken as proportional to the resistance of that part of the intervening plant, e.g., the difference between the readings for the oxide shafts and tower 1, is proportional to the resistance of the oxide coolers. The shaded areas show the relative resistance for all the important parts of the plant; the dotted line shows the curve for the Hereschoff unit. The proportionalities are not exact as the position with respect to the main fan determines to a small extent the pressure or suction apart from any intervening resistances.

It will be seen that the resistances of the absorption towers are approximately the same, and that the highest resistances are encountered in the oxide and platinum shafts (including the adjacent mains, &c.), the resistance of the air drying towers is also considerable. The amount for the oxide coolers is also large, but may be accounted for by the amount of gas main to be traversed, a factor which is included with the coolers. The same remark applies to the platinum shaft, where the resistance offered by the superheater forewarmer, heat exchange, and platinum cooler are included with the shaft itself.

Every manometer has been read every two days, and a tabulated and graphic record kept, thus it is possible to see at a glance when any given manometer was steadily altering, indicating a gradual change of resistance. In this way gradual chokes in the acid catchers, filters, and coolers have been detected.

# H.M. FACTORY QUEEN'S FERRY. — MANNHEIM OLEUM PLANT. RELATIVE RESISTANCES OF THE DIFFERENT PARTS OF THE PLANT.



Malby & Sons Ltd.

FIG. 8.

NOTE: SCALE 3/4" = 1' 0"



**The conversion of  $\text{SO}_2$  to  $\text{SO}_3$ .**—The conversion of  $\text{SO}_2$  to  $\text{SO}_3$  depends upon the following factors :—

- (1) Concentration of catalyst.
- (2) Temperature.
- (3) Composition of the burner gas.
- (4) Quality or condition of the catalyst

The concentration of the catalyst, or the quantity of the catalyst per unit volume of gas is determined by the amount put into the shaft and by the composition and speed of the gas. Up to the present the latter has been determined by the speed of the main fan, which has been constant and at its maximum, and the various resistances only alterable within narrow limits. The amount of oxide which can be employed in the oxide shaft is also limited. The quantity of platinum can be altered by changing the quantities during the platinising process (*vide infra*). Up to the present, it has had one part of platinum per 8.3 parts S (as  $\text{SO}_2$ ) per hour. Gaillo ratio (1 part Pt to 15 parts S).

The question of temperature has presented more difficulties. In view of the nature of the structure and position of the oxide shaft, it is impossible to keep the whole depth of oxide at the correct temperature; the lower layers may be at too high a temperature, as these meet the burner gas direct from the burner, but there is no evidence to show which zone of the catalyst is at the required temperature, since there are no facilities for taking a temperature in the oxide shaft.

The fact recently demonstrated that the dropping and filling operations temporarily lower the activity of the oxide may be due to a lowering of temperature.

With regard to the temperature control in the platinum shaft, the pyrometers only tell the temperature of the gas entering the shaft. The temperature of the issuing gas is of no great importance, because so long as the temperature for maximum conversion with the speed of gas is either not reached or exceeded in the gas leaving the platinum, so long will the efficiency suffer.

It has already been shown that to obtain the best results from the catalysts, they must be supplied with a constant burner gas containing about 5.5 per cent. of  $\text{SO}_2$ . The amount of oxygen that can be supplied to the burners cannot be increased beyond the maximum amount the main fan can draw, so that the higher the  $\text{SO}_2$  in the burner gas, the lower the oxygen. The higher the conversion in the oxide shaft, the lower the volume of  $\text{SO}_2$  going to the platinum, and consequently the lower the exit. The efficiency of platinum falls with the decrease in  $\text{SO}_2$  however, since lower concentrations of  $\text{SO}_2$  and oxygen produce a lower velocity of combination so that in proportion less is converted.

The condition of the platinum catalyst depends upon the platinising process, the purity of the gases, and the length of time it is in use.

Details of the platinising process are given below, together with some details of the life of the mat. The loss of activity is due in

practically every case to arsenic poisoning, the arsenic being carried to the platinum in the acid mist which the filters fail to remove.

**Asbestos mats.**—Many varieties of asbestos have been platinised with a view to finding which variety was most suitable for carrying the spongy platinum.

These might be described under three heads—

- (1) Blue asbestos.
- (2) White asbestos fibre supported by and wound round lengths of wire.
- (3) White asbestos.

The chief difficulty which has been encountered has been the disintegration caused by the action of the acid washes upon the asbestos fibre. In the case of the blue asbestos mentioned above, its solubility in HCl is only 15 per cent., and judged by this factor alone, it would seem to be a suitable substance for carrying the platinum. Unfortunately, on heating, blue asbestos turns a reddish-brown colour and becomes very brittle, thus rendering it unsuitable for the substance of a Mannheim mat.

*White asbestos supported by wire.*—This type of mat remained in good condition throughout the whole of the platinising process, but on being removed from the platinum shaft, the wires had gone (evidently converted to ferrous sulphate) and the strands of asbestos having lost their supports and not being strong enough to support their own weight, crumbled to pieces on being removed from the element of which it had formed a part.

*White asbestos.*—When platinising first commenced the mats were made of asbestos cord of  $\frac{1}{8}$  inch diameter, consisting of 12 strands of fibre. These mats turned out successfully and were not in the least brittle after passing through the platinising process. This stock of mats was followed by a stock of mats consisting of 36 strands of fibre. These mats fell to pieces before even the platinising process was finished. It was suggested that this might have been due to the fact that a large percentage of the magnesium in the mat had not been removed by the acid washes. A sample taken from one of these inferior mats showed only the slightest trace of magnesium, thus disproving that suggestion. The only other chemical cause for the disintegration was the fact that these mats were 60 per cent. soluble in hydrochloride so that during the HCl wash, a large percentage of the mat was removed and the skeleton remaining was not strong enough to stand any strain at all. But this solubility question applies equally to the asbestos used in the original mats, for its solubility was 59.42 per cent. and yet the mats were most satisfactory after platinising. This seems to point to the fact that it is only by a practical application to the asbestos of the platinising process that one may discover which one variety of asbestos is most suitable for platinising and that it is the physical rather than the chemical condition of the mat which influences its condition after platinising.

Analyses of mats before and after treatment gave the following results:—

<i>Before Treatment.</i>			
Blue asbestos.		White asbestos.	
SiO <sub>2</sub>	55.10	SiO <sub>2</sub>	38.25
FeO	17.90	FeO	9.61
Fe <sub>2</sub> O <sub>3</sub>	19.81	MgO	39.54
Na <sub>2</sub> O	7.10	H <sub>2</sub> O	12.20
Sol. in HCl	7.56	Sol. in HCl	59.42
" H <sub>2</sub> SO <sub>4</sub>	5.89	" H <sub>2</sub> SO <sub>4</sub>	58.09
Loss on ignition	1.95		
<i>After Treatment.</i>			
Blue asbestos.		White asbestos.	
SiO <sub>2</sub>	63.70	SiO <sub>2</sub>	70.53
FeO	14.63	FeO	4.35
Fe <sub>2</sub> O <sub>3</sub>	16.26	Fe <sub>2</sub> O <sub>3</sub>	4.72
Na <sub>2</sub> O	5.41	MgO	13.49
Sol. in HCl	12.30	H <sub>2</sub> O	6.91
" H <sub>2</sub> SO <sub>4</sub>	7.37	Sol. in HCl	25.71

Later deliveries of asbestos mats have consisted of mats of a various number of strands (32, 16, 38). All these mats have stood the platinising process well, and from this, it seems that the number of strands of fibre which make up the asbestos cord is immaterial but that the physical quality of the asbestos is all that matters.

*Method of platinising.* Forty litres of pure distilled water are placed in an enamelled bath. To this is added 1 litre of Na<sub>2</sub>CO<sub>3</sub> solution (containing  $\frac{3}{8}$  lb. Na<sub>2</sub>CO<sub>3</sub>). The whole is heated to boiling point by steam at about 20 lb. pressure, and an asbestos mat is then placed in the bath as soon as the liquid boils vigorously. One litre of HCOONa sol. (containing 1 lb. HCOONa (pure) per litre) is added. The liquid is again brought to boiling point and 400 c.c. of 10 per cent. PtCl<sub>4</sub> sol. (previously made alkaline with Na<sub>2</sub>CO<sub>3</sub> sol.) are poured in slowly. The mat is moved up and down through the solution three or four times and then a cover is placed on the bath and the liquid allowed to boil for a quarter of an hour. The mat is then reversed and a further 200 cc of PtCl<sub>4</sub> sol. added and the solution is then kept at boiling point till the whole of the platinum is deposited on the mat, and the liquid clear completely. The mat is then removed and placed in another enamelled bath containing distilled water, until 10 mats are completed. After four or five hours, the water is run off and replaced by a 10 per cent sulphuric acid wash at a temperature of 35–40° C. This first acid wash should last about 18 hours, and is followed by a second 10 per cent sulphuric acid wash also lasting 18 hours at the same temperature. The acid treatment is then followed by two hot-water washings each lasting 10–12 hours, which remove the soluble sulphates formed during the sulphuric acid treatment.

The mats are then placed on wooden racks to drain and dry in current of air. After drying they are ready to be mounted for

baking in the platinum shaft. This baking should last five or six hours. After baking the element is dismantled and the mats put into pure distilled water and are left there until they are quite pliable; after which they are given a 5 per cent. hot hydrochloric treatment ( $45^{\circ}\text{C}.$ ) of at least 12 hours.

After this follow two hot water washings each lasting six hours, and, finally, on cold water wash lasting about the same time.

The mats are then drained on racks and sprinkled with cold distilled water until the water draining from the mats shows no trace of chloride or sulphate. It is important to test the distilled water continually, for the presence of any impurity affects the deposition and the adherence of the platinum black on the asbestos. It is also essential to keep the liquid up to boiling point throughout the whole of the platinising process.

*Re-treatment removal of arsenic.* After an element is removed from the plant samples from the third and sixth mats are taken and the percentage of As determined. The mats are then given a 5 per cent. hydrochloric acid wash at  $60^{\circ}\text{C}.$  for six hours. They are then washed twice in hot water and finally drained and sprayed with distilled water till the water issuing from the mats shows no trace of sulphate or chloride. The mats are then dried and samples again taken to determine the As in the retreated mat.

**Heat balance.** On the section on which experimental work with the burners was carried out, arrangements were made for a number of special observations to be recorded, more particularly with regard to temperatures at different points in the gas circulation.

In addition to the ordinary continuous records of superheater temperatures, composition of exit gases, conversion, &c., continuous readings were taken of the temperature of gases entering forewarmers from oxide shafts, leaving forewarmer for oxide cooler Nos. 1 and 2, leaving oxide coolers Nos. 1 and 2, entering heat exchangers from filters, leaving heat exchangers for forewarmers, leaving forewarmers for superheaters, leaving platinum shafts for heat exchangers, and leaving heat exchangers for platinum coolers. Special holes and tubes for pyrometers were introduced where required.

Working data for the period March 2nd to April 20th, 1918, are shown in the accompanying graphs (Fig. 8A).

The average data for the various temperatures and gas compositions for the period March 2nd to April 2nd, are made use of for heat calculation. In the case of gas compositions and conversions, hourly tests were carried out over the whole of the period, and in the case of temperatures, these were either continuously recorded, or read hourly.

Pyrites burnt per 24 hours, 5.6 tons.

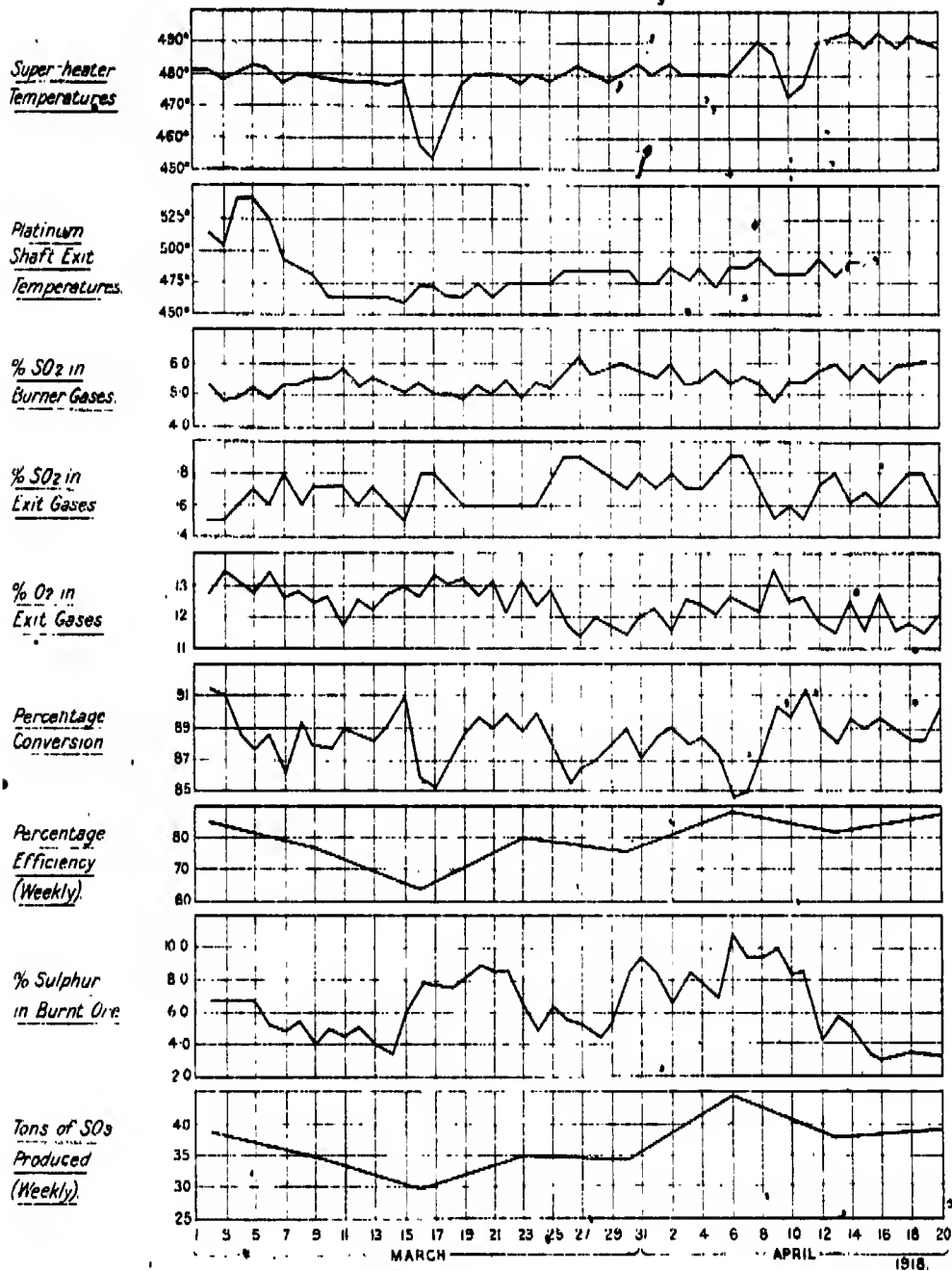
Sulphur content of burnt ore, 5 per cent.

Coke burnt in superheater per 24 hours (calorific value taken as 6,000), 1.9 tons.

Moisture in air entering burners, 0.30 grams per cub. metre.

Burner gas, 5.4 per cent.  $\text{SO}_2$ , 13.7 per cent.  $\text{O}_2$  (by vol.).

# H. M. FACTORY QUEEN'S FERRY: MANNHEIM OLEUM PLANT.



NOTE I. Pyrometers in Exits from Platinum Shafts were reading incorrectly for the first week of March.

NOTE II. The very high Sulphur content of about 8<sup>th</sup> to 10<sup>th</sup> April is to be attributed to a good deal of unburnt ore falling through the bars during the operation of removing a number of clinkers, and is not representative.

NOTE III. Efficiency and Production are shewn weekly, so do not shew so much direct connection with other figures.

FIG. 8A





Exit gas, 0.7 per cent.  $\text{SO}_2$ , 12.4 per cent.  $\text{O}_2$  (by vol.).

Oxide conversion, 40 per cent.

Total conversion, 88.1 per cent.

Temperature of gas leaving oxide shafts for forewarmers -	510° C.
Temperature of gas leaving forewarmers for Nos. 1 and 2 oxide coolers -	365° C.
Temperature of gas leaving Nos. 1 and 2 oxide coolers for No. 3 oxide coolers -	159° C.
Temperature of gas leaving No. 3 oxide cooler for No. 1 absorption tower -	65° C.
Temperature of gas leaving filters for heat exchangers -	15° C.
Temperature of gas leaving heat exchangers for forewarmers -	240° C.
Temperature of gas leaving forewarmers for superheaters -	376° C.
Temperature of gas leaving superheaters for platinum shafts -	478° C.
Temperature of gas leaving platinum shafts for heat exchangers -	480° C.*
Temperature of gas leaving heat exchanger for platinum coolers -	230° C.
Temperature of gas leaving platinum cooler for No. 3 absorption towers -	80° C.

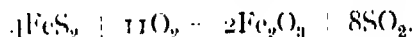
*Other data used.*

Cal. per Kg.

Specific heat at constant pressure of $\text{O}_2$ -	0.2158
Specific heat at constant pressure of $\text{N}_2$ -	0.2459
Specific heat at constant pressure of $\text{SO}_2$ -	0.1544
Specific heat at constant pressure (gas) of $\text{SO}_3$ -	0.24
Specific heat of burnt pyrites -	0.2
Calorific value of pyrites -	2,915 Cal. per Kg. sulphur burnt.

(Sommermeier, *J. Amer. Chem. Soc.*, 1914, 36, 555.)

It has been assumed that all sulphur in the pyrites is present in the form of  $\text{FeS}_2$  (as the ore contains 47 per cent. S, it is therefore assumed to consist of 88.1 per cent.  $\text{FeS}_2$ ); also that sulphur in the residues is present as  $\text{FeS}$ ; further that the reaction in the burners is according to the equation



In addition, the weight of the burnt ore residue is taken to be 75 per cent. of the weight of unburnt pyrites.

\* In the case of this section the pyrometer extended along the inside of the pipe leaving the platinum shaft. In the case of another section running during the period over which these observations extend, under precisely similar conditions, the pyrometer extended straight in over the topmost element of platinized asbestos, and this showed a mean temperature of 500° C.

There is no doubt but that in the first case the temperature in the top of the shaft itself was about 500° C., and that the lower temperature of the gas in the pipe leaving the shaft was due to leaking of heat along that section of pipe.

Burner gas contains 5.4 per cent.  $\text{SO}_2$  and 13.7 per cent.  $\text{O}_2$   
0.9 per cent.  $\text{N}_2$ .

$$\begin{aligned}\text{S burnt per 24 hours} &= (5.6 \times .47) - (5.6 \times .75 \times .05) \times 2240. \\ &= 5,425 \text{ lb. S.} \\ &= 10,850 \text{ lb. SO}_2.\end{aligned}$$

$$\therefore \frac{358 \times 10,850}{64} = 60,700 \text{ cu. ft. SO}_2 \text{ at N.T.P.}$$

$$\frac{60,700 \times 2,885}{273} = 64,100 \text{ cu. ft. SO}_2 \text{ at 15.5.}$$

Nitrogen entering burners—

$$\begin{aligned}\frac{80.9 \times 64,100}{5.4} &= 960,000 \text{ cu. ft. N}_2 \text{ at 15.5.} \\ &= 908,600 \text{ cu. ft. N}_2 \text{ at NTP.}\end{aligned}$$

Air entering burners per 24 hours ( $\text{N}_2$  79.3 per cent.)—

$$\frac{100 \times 960,000}{79.3} = 1,211,000 \text{ cu. ft. air at 15.5.}$$

Vol. gas leaving ( $\text{N}_2$  86.9 per cent.)—

$$\frac{79.3 \times 1,211,000}{86.9} = 1,105,000 \text{ cu. ft. gas at 15.5.}$$

Vol. of  $\text{O}_2$ —

$$\frac{13.7 \times 60,700}{5.4} = 154,000 \text{ cu. ft. O}_2 \text{ at NTP.}$$

Weight of  $\text{O}_2$ —

$$\frac{32 \times 154,000}{358} = 13,760 \text{ lb. O}_2.$$

Weight of  $\text{N}_2$ —

$$\frac{28 \times 908,600}{358} = 71,000 \text{ lb. N}_2.$$

Thus leaving burners per 24 hours—

$$\text{SO}_2 = 10,850 \text{ lb.}$$

$$\text{O}_2 = 13,760 \text{ lb.}$$

$$\text{N}_2 = 71,000 \text{ lb.}$$

Forty per cent. of  $\text{SO}_2$  is converted in oxide shafts (including conversion in burners themselves, by action of brickwork, &c.), so leaving oxide shafts per 24 hours are—

$$6,510 \text{ lb. SO}_2$$

$$5,430 \text{ lb. SO}_3$$

$$12,610 \text{ lb. O}_2$$

$$71,000 \text{ lb. N}_2$$

The  $\text{SO}_3$  is absorbed in towers 1 and 2, so gases passing from filters through heat exchangers, forewarmers and superheaters to platinum shafts per 24 hours are :—

$$6,510 \text{ lb. SO}_2$$

$$12,610 \text{ lb. O}_2$$

$$71,000 \text{ lb. N}_2$$

Over all conversion is 88.1 per cent.; gases leaving platinum shafts per 24 hours are :—

1,290 lb.  $\text{SO}_2$   
 6,520 lb.  $\text{SO}_3$   
 11,320 lb.  $\text{O}_2$   
 71,000 lb.  $\text{N}_2$

These figures are utilised in the following calculations.

(NOTE.—Any  $\text{SO}_2$  dissolved in circulating acids, and  $\text{SO}_3$  condensing in coolers, is neglected.)

It is assumed that the average atmospheric temperature is  $15^\circ \text{C.}$ , and for the purpose of these calculations  $15^\circ \text{C.}$  is taken as the zero of temperature.

*Heat balance.*

<i>Heat generated in C.H.U. per 24 hours.</i>		<i>Heat given up in C.H.U. per 24 hours.</i>	
By combustion of		In Nos. 1 and 2 oxide	
pyrites - - -	15,800,000	coolers - - -	4,619,700
By conversion in		In No. 3. oxide cooler	2,113,000
oxide shafts - -	1,529,000	In Nos. 1 and 2 absorption towers acid	
*By conversion in		catchers and filters	1,122,300
platinum shafts -	1,839,000	In platinum cooler -	3,240,370
By superheater -	29,380,000	In Nos. 3, 4 and 5 absorption towers and in exit gases -	1,404,330
		In oxide removed from burners and oxide shafts -	72,170
		In moisture introduced in oxide -	3,605
		In moisture introduced in pyrites -	8,500
		In radiation from heat exchangers - -	656,300
		In radiation from superheaters and in waste gases from superheater stacks -	27,099,200
		In radiation from burners and oxide shafts - - -	8,547,000
Total -	<u>48,548,000</u>	Total -	<u>48,886,475</u>
		Excess -	<u>338,475</u>

*Calculations**I.—Combustion of pyrites.*

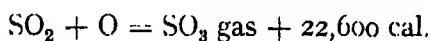
5.6 tons per day containing 47 per cent. S, residue 75 per cent. weight of the unburnt ore, containing 5 per cent. S. Calorific value, 2,915 C.H.U. per lb., S burnt.

Heat generated

$$= 5.6 \times 2240 \times 0.47 \times 2915 - 5.6 \times 2240 \times 0.05 \times 2915.$$

$$= 17,170,000 - 1,370,000 \text{ C.H.U. per 24 hours.}$$

$$= 15,800,000 \text{ C.H.U.}$$

*II.—Conversion in oxide shafts.*

$$\text{Heat generated} = \frac{5.413 \times 22,600}{80} = 1,529,000 \text{ C.H.U.}$$

*III.—Conversion in platinum shafts.*

$$\text{Heat generated} = \frac{6.514 \times 22,600}{80} = 1,839,000 \text{ C.H.U.}$$

*IV.—Superheaters.*

Gas enters superheaters at 370° and leaves at 478°. Temp. diff., 108°.

Heat taken up N <sub>2</sub> , 71,000 × 108 × 0.2459	= 1,885,000 C.H.U.
SO <sub>2</sub> , 6,510 × 108 × 0.1544	= 108,600 „
O <sub>2</sub> , 12,610 × 108 × 0.2158	= 293,800 „
	2,287,400 „

Superheaters burn 1.9 tons of coke per 24 hours (cal value, 6,900).

$$\text{Heat supplied, } 1.9 \times 2,240 \times 6,900 = 29,380,000 \text{ „}$$

$$\text{Efficiency of superheaters} = \frac{2287}{2938} = 7.8 \text{ per cent.}$$

$$\begin{array}{l} \text{Loss in gases leaving superheater stacks and} \\ \text{in radiation} \end{array} = 27,092,600 \text{ „}$$

*V.—Oxide coolers.*

The “oxide” coolers are so called because they cool the gas from the oxide shafts.

Gases leave forewarmer chambers at 365° and leave Nos. 1 and 2 coolers at 159° and No. 3 cooler at 65°.

Total heat in gases leaving forewarmer—

SO <sub>2</sub> 6,510 × 350 × 0.1544	= 351,800 C.H.U.
SO <sub>3</sub> 5,430 × 350 × 0.24	= 456,000 „
O <sub>2</sub> 12,610 × 350 × 0.2158	= 952,200 „
N <sub>2</sub> 71,000 × 350 × 0.2459	= 6,110,000 „
Total	7,870,000 „

Total heat removed by Nos. 1 and 2 coolers. Temp. diff.,  
 $365 - 159 = 206^{\circ}$ .

SO <sub>2</sub>	6,510	$\times 206$	$\times 0.1544$	-	-	=	207,100	C.H.U.
SO <sub>3</sub>	5,430	$\times 206$	$\times 0.24$	-	-	=	268,300	"
O <sub>2</sub>	12,610	$\times 206$	$\times 0.2158$	-	-	=	550,800	"
N <sub>2</sub>	71,000	$\times 206$	$\times 0.2459$	-	-	=	3,598,000	"
Total	-	-	-	-	-		<u>4,634,200</u>	"

Efficiency of coolers 1 and 2,  $\frac{4,634,200 \times 100}{7,870,000} = 58.9$  per cent.

Heat transference, 500 C.H.U. per square foot per hour.

Surface of one cooler = 192 square feet.

Total heat removed by No. 3 cooler. Temp. diff.,  $159 - 65 = 94^{\circ}$ .

SO <sub>2</sub>	6,510	$\times 94$	$\times 0.1544$	-	-	=	94,500	C.H.U.
SO <sub>3</sub>	5,430	$\times 94$	$\times 0.24$	-	-	=	122,600	"
O <sub>2</sub>	12,610	$\times 94$	$\times 0.2158$	-	-	=	255,800	"
N <sub>2</sub>	71,000	$\times 94$	$\times 0.2459$	-	-	=	1,641,000	"
Total	-	-	-	-	-		<u>2,113,900</u>	"

Efficiency of No. 3 cooler,  $\frac{100 \times 2,113,900}{7,870,000 - 4,634,200} = 65.3$  per cent.

Heat transference = 459 C.H.U. per square foot per hour.

The remaining  $(7,870,000 - 4,634,200 - 2,113,900) = 1,121,900$  C.H.U. are lost in the absorption and filter system, the average temperature of the gas leaving the filters being  $15^{\circ}$ .

*Note.*—No account is taken of certain other factors entering into heat reaction in the coolers, such as condensation of steam, heat of combination of SO<sub>3</sub> and H<sub>2</sub>O and heat of dilution of H<sub>2</sub>SO<sub>4</sub> so formed, which are considered small enough to be negligible.

#### VI.—Heat exchangers and forewarmers.

The cold unconverted gases enter the heat exchangers at  $15^{\circ}$  and leave at  $240^{\circ}$ . The hot gases from the converters leave the converters at  $480^{\circ}$  and leave the heat exchangers at  $230^{\circ}$ .

##### *Heat taken up by cold gases.*

SO <sub>2</sub>	6,510	$\times 225$	$\times 0.1544$	-	-	=	226,200	C.H.U.
O <sub>2</sub>	12,610	$\times 225$	$\times 0.2158$	-	-	=	612,600	"
N <sub>2</sub>	71,000	$\times 225$	$\times 0.2459$	-	-	=	3,928,000	"
Total	-	-	-	-	-		<u>4,766,800</u>	"

*Heat given up by hot gases.*

SO <sub>2</sub>	1,290 × 250 × 0.1544	-	-	=	49,810 C.H.U.
SO <sub>3</sub>	6,520 × 250 × 0.24	-	-	=	391,200 "
O <sub>2</sub>	11,320 × 250 × 0.2158	-	-	=	611,000 "
N <sub>2</sub>	71,000 × 250 × 0.2459	-	-	=	4,364,000 "
Total	-	-	-	-	<u>5,416,010 "</u>

$$\text{Efficiency, } \frac{4,766,800 \times 100}{5,416,010} = 87.9 \text{ per cent.}$$

Heat transference = 400 C.H.U. per square foot surface per hour.

Heat lost by radiation from pipes between converters and heat exchangers and from surface of heat exchangers = 5,416,010 - 4,766,800 = 649,200, or 105 C.H.U. per square foot per hour.

*Forewarmers.*—Cold gases enter forewarmers at 240° and leave at 370°. Hot gases enter forewarmers at 510° and leave at 365°.

Heat taken up by cold gases. Temp. diff., 130°.

SO <sub>2</sub>	6,510 × 130 × 0.1544	-	-	=	130,700 C.H.U.
O <sub>2</sub>	12,610 × 130 × 0.2158	-	-	=	353,700 "
N <sub>2</sub>	71,000 × 130 × 0.2459	-	-	=	2,270,000 "
Total	-	-	-	-	<u>2,754,400 "</u>

Heat given up by hot gases. Temp. diff. = 145°—

SO <sub>2</sub>	6,510 × 145 × 0.1544	-	-	=	145,700 C.H.U.
SO <sub>3</sub>	5,430 × 145 × 0.24	-	-	=	189,100 "
O <sub>2</sub>	12,610 × 145 × 0.2158	-	-	=	394,700 "
N <sub>2</sub>	71,000 × 145 × 0.2459	-	-	=	2,531,000 "
Total	-	-	-	-	<u>3,260,500 "</u>

$$\text{Efficiency, } \frac{2,754,400 \times 100}{3,260,500} = 84.5 \text{ per cent.}$$

Heat transference, 135 C.H.U. per square foot per hour.

VII.—*Platinum cooler.*

The "platinum" cooler is so called because it cools the gases from the platinum shaft.

Gases leave heat exchangers at 230°. Temp. diff. = 230 - 15 = 215°. Total heat in gases leaving heat exchangers—

SO <sub>2</sub>	1,290 × 215 × 0.1544	-	-	=	42,820 C.H.U.
SO <sub>3</sub>	6,520 × 215 × 0.24	-	-	=	336,600 "
O <sub>2</sub>	11,320 × 215 × 0.2158	-	-	=	525,200 "
N <sub>2</sub>	71,000 × 215 × 0.2459	-	-	=	3,751,000 "
Total	-	-	-	-	<u>4,655,620</u>

Heat removed in cooler. Temp. diff.,  $230 - 80 = 150^{\circ}$ .

SO <sub>2</sub>	$1,290 \times 150 \times 0.1544$	-	=	29,900	C.H.U.
SO <sub>3</sub>	$6,520 \times 150 \times 0.24$	-	=	234,800	"
O <sub>2</sub>	$11,320 \times 150 \times 0.2158$	-	=	357,300	"
N <sub>2</sub>	$71,000 \times 150 \times 0.2459$	-	=	2,619,000	"
Total	-	-	-	<u>3,241,000</u>	"

- Efficiency,  $\frac{3,241,000 \times 100}{4,655,600} = 69.6$  per cent.

Heat transference, 704 C.H.U. per square foot per hour.

The remaining 1,414,620 C.H.U. leaving the "platinum cooler" is lost in No. 3, 4, and 5 absorption towers and in exit gases.

#### VIII.—Oxide removed.

Eight hundred and ninety-six lb. are dropped from the four oxide shafts per 24 hours, also  $5.6 \times 0.75$  tons oxide are dropped from burner hoppers per 24 hours. This is assumed to leave burners at an average temperature of  $50^{\circ}$  C. and the specific heat of oxide is taken as 0.2. Then heat removed per 24 hours  $= 5.6 \times 0.75 \times 2,240 \times 0.2 \times 35 + 896 \times 35 \times 0.2 = 65,900 + 6,270 = 72,170$  C.H.U.

#### IX.—Moisture.

Moisture in air entering burners

$= 0.3$  gram per c. metre.

$= \frac{0.3}{453.6 \times 35.315}$  lb. per cubic foot.

$= \frac{0.3 \times 1,211,000}{453.6 \times 35.315}$  lb. per 24 hours.

Taking specific heat of water vapour as 0.46. This vapour leaves oxide shafts at  $365^{\circ}$  C.

Heat removed  $= \frac{0.3 \times 1,211,000 \times 350 \times 0.46}{453.6 \times 35.315}$   
 $= 3,605$  C.H.U. per 24 hours.

Moisture introduced in oxide (into oxide shafts) which contains 0.08 per cent. H<sub>2</sub>O

$= 896 \times 0.0008$  per 24 hours  
 $= 0.72$  lb.

Moisture introduced in pyrites (0.085 per cent. H<sub>2</sub>O)

$= 5.6 \times 2,240 \times 0.00085$  lb. per 24 hours  
 $= 10.66$  lb.

∴ Total water introduced in oxide and pyrites per 24 hours  
 $= 11.38$  lb. entering at  $15^{\circ}$  C. leaving at  $365^{\circ}$  C.

Heat removed  $= 11.4 \times 85 + 11.4 \times 338 + 11.4 \times 265 \times 0.46$   
 $= 970 + 6,140 + 1,390$  C.H.U.  $= 8,500$  C.H.U.



X.—*Radiation.*

An allowance for radiation from surfaces of burners, oxide shafts, and forewarmers exposed to the air can be made only very approximately. The walls are of brick, coated in places with a layer of Kieselguhr, the whole covered with steel plate.

The temperature varies considerably on the outside, from 105° C. outside the lower door of platinum shaft through 85° C. to 55° C. near top of oxide shafts. Inside, too, the temperature varies from place to place. (The temperatures at different depths in the oxide shaft are shown in Fig. 8B.)

It has been assumed that the average temperature inside is 500° C., and the average temperature outside is 60° C., further, that transfer of heat takes place much as it would were the medium separating the inside from the outside a 15 inch brick wall.

According to Kent, under these conditions, the flow of heat through the wall would be 0.3 C.H.U. per square foot per hour per degree difference of temperature, *i.e.*, loss of heat between 500° C. and 60° C. would be 132 C.H.U. per square foot per hour.

Total surface of burners, oxide shafts, &c. (including hoppers in cellars) exposed to air in one section = 2,694 square feet.

∴ Total loss of heat per 24 hours =  $132 \times 2,694 \times 24$  C.H.U. = 8,547,000 C.H.U.

*Conclusions.*—Heat losses in the heat exchangers and from burners and oxide shafts are not excessive under the circumstances, being 105 and 132 C.H.U. per square foot per hour respectively. The greatest loss of heat occurs in the superheater; it would be possible to diminish this somewhat by lagging the superheater, but it is very questionable whether the saving of heat would repay the cost of installation.

It is most striking that the heat taken up by the gases passing through the superheater pipes is only 2,280,000 C.H.U. per 24 hours, whereas the gases leaving the forewarmer chamber carry with them 7,855,000 C.H.U. per 24 hours, and those leaving the heat exchangers carry 4,644,700 C.H.U. per 24 hours, all of which is waste heat, to be dissipated in the coolers, absorption towers, &c.

If little over 18 per cent. of this waste heat could be imparted to the purified gases before entering the platinum shaft, it would be possible to do away with superheaters altogether and to run regeneratively. It is true that the temperature to which it is desired to bring the gases (480° C.) is very near the temperature above the topmost element in the platinum shaft (500° C.), and no doubt, in the existing plant, suitable alterations would be so difficult and costly that the attempt would not be feasible, but if the design were altered in some way such that the entering gases could be passed round and between the platinum elements, with an arrangement for by-passing, so that the quantity brought in contact with the platinum chamber could be varied at will, there is little doubt that not only could more waste heat be utilised, but also that a new factor for controlling the temperature of the platinum shaft would be introduced, which would be easier to



## H. M. FACTORY QUEEN'S FERRY.

DIAGRAM TO SHOW VARIATION OF TEMPERATURE  
WITH DEPTH IN OXIDE SHAFTS.

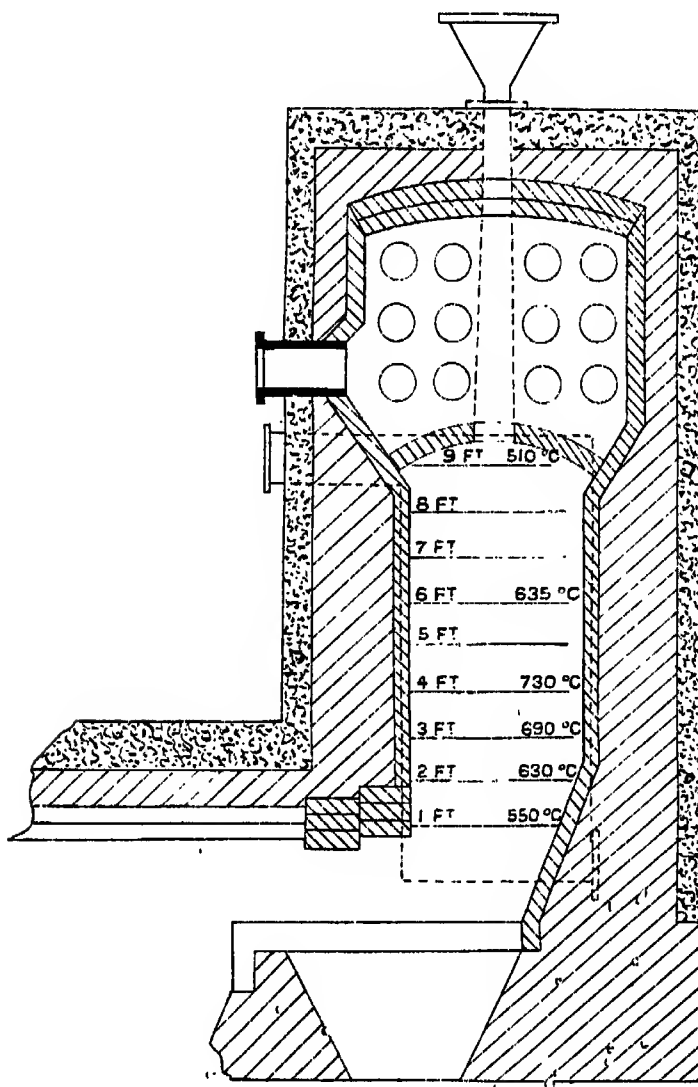


FIG. 8<sup>a</sup>

operate and much more rapid in effect than a superheater fire, with the probable result of marked improvement to conversion.

If the Fig. 8B showing oxide shaft temperatures be glanced at, it will be seen that half way down the oxide shaft temperatures in the neighbourhood of  $700^{\circ}\text{C}$ . are obtained; if a portion of the purified gases were arranged to pass through pipes well down in the oxide shafts, it should be readily possible to raise the mean temperature of the gases entering the platinum shaft to the desired point. Possibly it would be easier to run regeneratively if more pyrites was burnt per 24 hours. (Accounts have been heard of other plants which burn up to 10 and 12 tons per 24 hours, but hitherto attempts to increase the amount burnt to any extent by speeding up the main fan, have been singularly unsuccessful.)

As has been pointed out, the ratio of  $\text{SO}_2$  to platinum on the Mannheim plant is a very high one. With mats each carrying 24 grams platinum (1,440 grams or 3.17 lb. to the section) and a gas which carries 6,500 lb.  $\text{SO}_2$  through the platinum shafts per 24 hours, the ratio of  $\text{SO}_2$  per hour to platinum is 85 to 1.

This is about the maximum figure at which the Mannheim plant, as at present designed, can be run, and the optimum temperature would appear to be in the neighbourhood of  $500^{\circ}\text{C}$ .

There would seem to be good reason for increasing the proportion of platinum in the Mannheim unit, both to secure a higher maximum conversion, and a lower optimum temperature, when without doubt the plant, with some alterations, could be run regeneratively. It is highly desirable that a converter be arranged to carry the platinum in some form other than platinized asbestos.

The unsatisfactory nature of the asbestos mat has been referred to as well as the great waste involved in the re-treating process.

The experience gained in the Mannheim and Grillo plants using asbestos mats and granulated magnesium sulphate respectively as the carrier of the platinum showed great advantage in favour of magnesium sulphate and in ease and economy when the contact mass had to be retreated.

#### METHOD FOR CALCULATING THE PERCENTAGE CONVERSION AND THE PERCENTAGE COMPOSITION OF THE BURNER GASES FROM THE PERCENTAGE OF OXYGEN AND OF SULPHUR DIOXIDE IN THE GASES AFTER ABSORPTION OF THE SULPHUR TRIOXIDE

In the Mannheim plant the use of the method employed in the Grillo plant for determining the percentage of conversion of  $\text{SO}_2$  into  $\text{SO}_3$  is open to the objection that it is very difficult to obtain a fair sample of the burner gas entering the ferric oxide converter. This difficulty is avoided in the following alternative method of deducing the percentage of conversion and also the percentage of  $\text{SO}_2$  in the burner gas, from a determination of the percentage of  $\text{SO}_2$  and  $\text{O}_2$  in the gases leaving the converter.

In applying this method the percentage of  $\text{SO}_2$  in the gases leaving the converter may be determined as usual by Reich's method. To determine the percentage of oxygen a portion of the gas leaving the converter is freed from  $\text{SO}_2$  and  $\text{SO}_3$  by passing it through some suitable reagent such as iodine and caustic soda, and the percentage of oxygen is determined in the residual gas. This percentage after correction to the dry state and for temperature and pressure if necessary, is multiplied by  $(100 - \text{per cent. } \text{SO}_2)$  when the percentage of oxygen in the gases

200

leaving the converter is obtained. In both cases the presence of  $\text{SO}_3$  in the original gas is ignored, as the  $\text{SO}_3$  is liquified at once in contact with water vapour and does not affect the measured volume.

In the following study formulæ are developed for calculating the percentage conversion of sulphur dioxide to sulphur trioxide from the amount of oxygen and sulphur dioxide found in the exit gases from the Mannheim plant.

As far as is known these formulæ have never been worked out fully before. The method is used on this plant and seems to be the only successful technical method of getting the conversion over a period. The accuracy of the method of course depends on how nearly the equation  $4\text{FeS}_2 + 11\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$  expresses the reaction taking place in the burners. There seems to be no data on this point, but it is at least certain that the method of determining the conversion is as accurate as any other that has been tried at Queen's Ferry.

These formulæ enable the percentage conversion of  $\text{SO}_2$  to  $\text{SO}_3$  and the percentage of oxygen and  $\text{SO}_2$  in the burner gas to be calculated from an analysis of the exit gases.

In the case of sulphur being burnt to supply  $\text{SO}_2$  the formulæ given would be exact if the sulphur were pure; this is very nearly approximated to, usually, as the sulphur burnt does not contain much combustible impurity and incombustible impurities do not matter.

In the case of pyrites the formulæ would be rigidly true if the pyrites were pure  $\text{FeS}_2$  and burnt to  $\text{Fe}_2\text{O}_3$  only. Pena pyrites is fairly pure, so inaccuracies due to impurities are small, but there remain those due to (1)  $\text{FeS}$ ,  $\text{Fe}_3\text{O}_4$  and, perhaps,  $\text{FeO}$ ; and (2)  $\text{FeSO}_4$ , being in the cinders. (1) and (2) to some extent compensate one another, but (2) always seems to preponderate so that actually it requires more oxygen to produce 1 vol.  $\text{SO}_2$  than is given by the equation  $4\text{FeS}_2 + 11\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$ .

There is no data available regarding the actual relation of oxygen to  $\text{SO}_2$ , but it is believed that the formula given is not far wrong. The tables have been calculated on this formula. If " $r$ " be greater than 1.375 the conversion and the  $\text{SO}_2$  given by the tables will be greater than the true values. The formula may, of course, be used to determine the conversion in the oxide shaft on the Mannheim plant, the gas analysed being, in this case, that leaving the filters.

All formula assume complete absorption of  $\text{SO}_3$ . Except in abnormal cases this is so nearly the case as to make the error due to it inappreciable.

Consider 100 vols. of air passing into the burners :—

Let  $r$  = vol. oxygen used up in the production of 1 vol.  $\text{SO}_2$ .

„  $x$  = vol.  $\text{SO}_2$  in gas passing from the burners.

„  $y$  = vol.  $\text{SO}_2$  converted into  $\text{SO}_3$ .

„  $a$  = percentage  $\text{SO}_2$  in gas analysed

„  $b$  = percentage  $\text{O}_2$  in gas analysed.

Then percentage conversion =  $100 y/x$ .

In the Burner Gases :—

Vol.  $\text{O}_2$  used up - - - =  $rx$ .

∴ Vol.  $\text{O}_2$  remaining - - - =  $21 - rx$ .

Vol. of  $\text{O}_2$  fixed as  $\text{Fe}_2\text{O}_3$  - - - =  $rx \cdot x = x(r - 1)$ .

Total vol. of gases - - - =  $100 - x(r - 1)$ .

∴ Percentage  $\text{SO}_2$  in burner gas - - - =  $\frac{100x}{100 - x(r - 1)}$ .

Percentage  $\text{O}_2$  in burner gas - - - =  $\frac{100(21 - rx)}{100 - x(r - 1)}$ .

After conversion and absorption of the  $\text{SO}_3$  we have—

$\text{SO}_2$  converted and absorbed - - - =  $y$ .

Since 1 vol. of  $\text{SO}_2$  requires  $\frac{1}{2}$  vol. of  $\text{O}_2$  to convert it into  $\text{SO}_3$ ,

the additional  $\text{O}_2$  used up - - - =  $y/2$ .

∴ Vol.  $\text{O}_2$  remaining - - - =  $21 - rx - y/2$ .

∴  $\text{SO}_2$  remaining - - - =  $x - y$ .

Since 2 vols. of  $\text{SO}_2$  combine with 1 vol. of  $\text{O}_2$  to form 2 vols. of  $\text{SO}_3$ ,

the total vol. of gases - - - =  $100 - x(r - 1) - 3y/2$ .

∴  $a = \frac{100(x - y)}{100 - x(r - 1) - 3y/2}$        $b = \frac{100(21 - rx - y/2)}{100 - x(r - 1) - 3y/2}$

From these equations we obtain :—

$$2x(ar - a + 100) + y(3a - 200) = 200a$$

$$ax(br - b - 100r) + y(3b - 100) = 200b - 4,200$$

Eliminating  $y$

$$x = \frac{200a(3b - 100) - (200b - 4,200)(3a - 200)}{2(ar - a + 100)(3b - 100) - 2(br - b - 100r)(3a - 200)}$$

$$= \frac{4,200 + 37a - 200b}{(100 - a - b)(1 + 2r)}$$

Eliminating  $x$

$$y = \frac{200a(br - b - 100r) - (200b - 4,200)(ar - a + 100)}{(3a - 200)(br - b - 100r) - (3b - 100)(ar - a + 100)}$$

$$= \frac{4,200 - 2a(21 + 79r) - 200b}{(100 - a - b)(1 + 2r)}$$

$$\therefore \text{Percentage conversion} = 100 \frac{y}{x} = 100 \left( \frac{4,200 - 2a(21 + 79r) - 200b}{4,200 + 37a - 200b} \right)$$

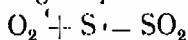
$$x = 100 \left[ 1 - \frac{79a(1 + 2r)}{4,200 + 37a - 200b} \right]$$

# MANNHEIM PROCESS

$$\begin{aligned}\text{Percentage SO}_2 \text{ in burner gas} &= \frac{100x}{100 - x(r-1)} \\ &= 100 \left[ \frac{4,200 + 37a - 200b}{100(142 + 158r) - 3a(21 + 79r) - 300b} \right]\end{aligned}$$

$$\begin{aligned}\text{Percentage O}_2 \text{ in burner gas} &= 100 \frac{(21 - rx)}{100 - x(r-1)} \\ &= 100 \left[ \frac{2,100 - a(21 + 79r) - b(21 - 158r)}{100(142 + 158r) - 3a(21 + 79r) - 300b} \right]\end{aligned}$$

*Burning Sulphur.*—When the source of SO<sub>2</sub> is sulphur, we have—



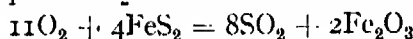
$$\therefore r = 1$$

$$\begin{aligned}\therefore \text{Percentage conversion} &= 100 \left[ \frac{4,200 - 200a - 200b}{4,200 + 37a - 200b} \right] \\ &= 100 \left[ 1 - \frac{237a}{4,200 + 37a - 200b} \right]\end{aligned}$$

$$\text{Percentage SO}_2 \text{ in burner gas} = \frac{4,200 + 37a - 200b}{3(100 - a - b)}$$

$$\text{Percentage O}_2 \text{ in burner gas} = \frac{2,100 - 100a \times 137b}{3(100 - a - b)}$$

*Burning pyrites.*—When the source of SO<sub>2</sub> is pyrites, assuming that it is pure FeS<sub>2</sub> and combustion is to Fe<sub>2</sub>O<sub>3</sub> and SO<sub>2</sub> only we have:—



$$\therefore r = \frac{11}{8} = 1.375$$

$$\begin{aligned}\therefore \text{Percentage conversion} &= 100 \left[ \frac{16,800 - 1,037a - 800b}{16,800 + 148a - 800b} \right] \\ &= 100 \left[ 1 - \frac{1185a}{16,800 + 148a - 800b} \right]\end{aligned}$$

$$\text{Percentage SO}_2 \text{ in burner gas} = 100 \left[ \frac{2}{3} \left( \frac{16,800 + 148a - 800b}{95,800 - 1,037a - 800b} \right) \right]$$

$$\text{Percentage O}_2 \text{ in burner gas} = 100 \left[ \frac{1}{3} \left( \frac{16,800 - 1,037a + 1,570b}{95,800 - 1,037a - 800b} \right) \right]$$

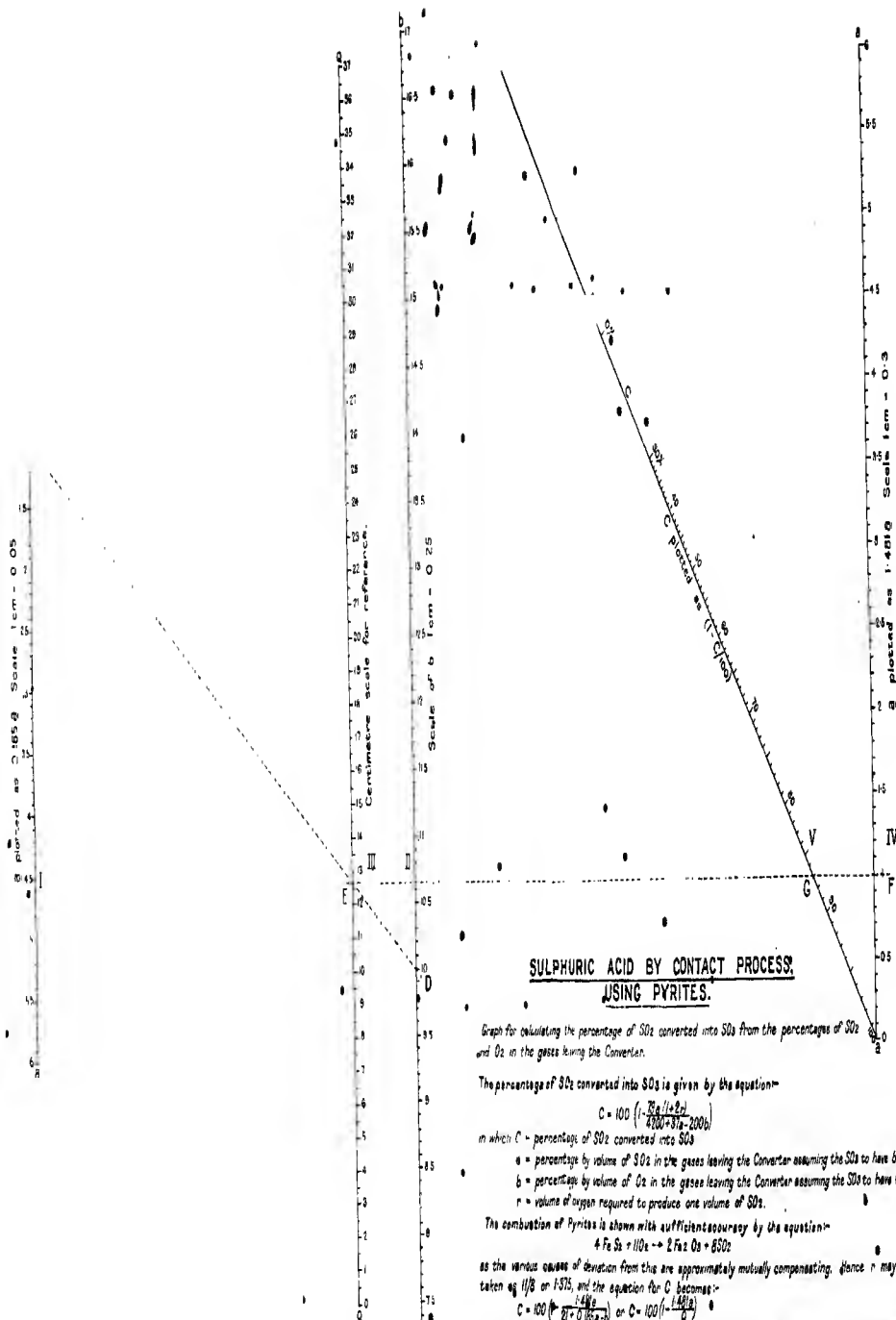








**SULPHURIC ACID BY CONTACT PROCESS, USING PYRITES.**  
 GRAPH FOR CALCULATING THE PERCENTAGE OF SO<sub>2</sub> CONVERTED INTO SO<sub>3</sub> FROM THE  
 PERCENTAGES OF SO<sub>2</sub> & O<sub>2</sub> IN THE GASES LEAVING THE CONVERTER



**SULPHURIC ACID BY CONTACT PROCESS,  
 USING PYRITES.**

Graph for calculating the percentage of SO<sub>2</sub> converted into SO<sub>3</sub> from the percentages of SO<sub>2</sub> and O<sub>2</sub> in the gases leaving the Converter.

The percentage of SO<sub>2</sub> converted into SO<sub>3</sub> is given by the equation:-

$$C = 100 \left( \frac{1 - \frac{a}{b}}{1 + \frac{a}{b} - \frac{200b}{400 + 31.6 - 200b}} \right)$$

in which C = percentage of SO<sub>2</sub> converted into SO<sub>3</sub>

- a = percentage by volume of SO<sub>2</sub> in the gases leaving the Converter assuming the SO<sub>3</sub> to have been liquified
- b = percentage by volume of O<sub>2</sub> in the gases leaving the Converter assuming the SO<sub>3</sub> to have been liquified.
- r = volume of oxygen required to produce one volume of SO<sub>3</sub>.

The combustion of Pyrites is shown with sufficient accuracy by the equation:-



as the various causes of deviation from this are approximately mutually compensating, hence r may be taken as 1/8 or 1.25, and the equation for C becomes:-

$$C = 100 \left( \frac{1 - \frac{a}{b}}{1 + \frac{a}{b} - \frac{1.25b}{1.25 - 1.25b}} \right) \text{ or } C = 100 \left( \frac{1 - \frac{a}{b}}{1 + \frac{a}{b} - \frac{1.25b}{1.25 - 1.25b}} \right)$$

To use the Graph place a straight-edge or a stretched thread on the value of a on axis I and on the value of b on axis II and note the point of intersection with axis III. Then join this point with the value of r on axis IV and read off the required percentage on axis V.

Example - Suppose a = 1 and b = 10. The first position of the straight-edge is shown by the line CD cutting the Q axis at E. The second position of the straight-edge is shown by the line EF and the intersection of EF with the C axis at G gives as result 86.6% which is the percentage required. The r scale on the Q axis is merely for reference.

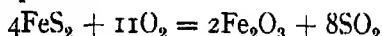
Note - a is found as usual by Reich's method. Since SO<sub>2</sub> is converted into H<sub>2</sub>SO<sub>4</sub> as an extract with water or water vapour, it does not contribute to the measured volume of gas.

To find b pass some of the gas leaving the converter through a suitable reagent to absorb SO<sub>2</sub> and SO<sub>3</sub>, and determine the percentage by volume of O<sub>2</sub> in the residual gas reduced to the dry state.

This percentage multiplied by  $\frac{100}{100 - b}$  gives b.

GRAPHS FOR CALCULATING PERCENTAGE CONVERSION OF SULPHUR DIOXIDE INTO SULPHUR TRIOXIDE, AND PERCENTAGE OF SULPHUR DIOXIDE IN THE BURNER GAS ACCORDING TO THE PRECEDING METHOD BY PROFESSOR WILSMORE

In applying the method to cases where the  $\text{SO}_2$  is obtained from pyrites, there is some uncertainty concerning the volume of oxygen used up to produce one volume of  $\text{SO}_2$ . The ideal combustion of pyrites is expressed by the equation



but in practice some sulphide will be left in the cinders, whilst, on the other hand, some sulphate will be formed; it is assumed, however, that these sources of error will in general be mutually compensating as regards the consumption of oxygen. If this be admitted, the equations when applied to the analysis of the gases from pyrites may be reduced to the following simple forms, which have been used for the graphs. If  $a$  is the percentage by volume of  $\text{SO}_2$  and  $b$  that of oxygen in the gases leaving the converter (assuming the  $\text{SO}_3$  to have been removed),  $C$  the percentage of conversion and  $S$  the percentage of  $\text{SO}_2$  in the burner gas, then:—

$$(1) \quad C = 100 \left( 1 - \frac{1.481a}{21 + 0.185a - b} \right)$$

$$(2) \quad S = 100 \left( \frac{21 + 0.185a - b}{179.6 - 1.944a - 1.5b} \right)$$

*Data for plotting and checking the graphs.*

I. *Percentage of conversion.*—Equation (1) may be written in the form—

$$(1 - C/100) = 1.481/Q$$

in which  $Q = (21 + 0.185a - b)$ . The calculation, therefore, consists of two operations, the first being to find the value of  $Q$ . The two  $a$  axes and the  $b$  axis must be parallel, but their distance apart and the scales used are merely matters of convenience. If the scales (namely, the number of units per unit of length) on the left-hand  $a$  axis, the  $b$  axis, the  $Q$  axis and the right-hand  $a$  axis are denoted by  $s_1$ ,  $s_2$ ,  $s_3$  and  $s_4$  respectively, then  $s_3$  must equal  $(s_1 + s_2)$  and the distances of the  $Q$  axis from the left-hand  $a$  axis and the  $b$  axis must be to each other as  $s_2$  to  $s_1$ . The left-hand  $a$  axis, as it represents a positive quantity in the denominator, is graduated downwards. The  $b$  axis representing a negative quantity in the denominator is graduated upwards. As  $Q$  is also in the denominator and is positive, its scale, if plotted, would run downwards.

In using the graph (Fig. 9) the actual values of  $Q$  are not wanted, but as in practice it is convenient to have a scale on the  $Q$  axis for reference, any decimal scale may be laid on it. As the right hand  $a$  axis represents a positive quantity in the numerator, its scale must be plotted

upwards, also  $a$  must be plotted on the left-hand scale as  $0.185a$ , and on the right-hand scale as  $1.481d$ . The C axis is drawn from the zero of the right-hand  $a$  scale to the true zero of the Q scale. If, however, the latter point is beyond the scope of the drawing board, an intermediate point on the C scale, say, that for  $C = 30$  per cent., may be found graphically from two corresponding pairs of values of  $a$  and  $b$  taken from the table below. The other chief points on the C scale may be found in the same way. If the length of the C axis can be accurately measured, the chief points on it can also be found from the relationship:—

$$z = \frac{d(s_4h - s_3)}{s_4h + s_3}$$

in which  $z$  is the distance of the point required from the centre of the C axis,  $d$  half the length of that axis,  $s_3$  and  $s_4$  the scales of the Q and right-hand  $a$  axes respectively, and  $h = (1 - C/100)$ . The C scale not being uniform, the smaller divisions on it must be inserted by projection from a decimal scale.

In this graph, Fig. 9,  $s_1 = 0.05$ ,  $s_2 = 0.25$ , and  $s_4 = 0.3$  units per cm. Consequently,  $s_3 = (s_1 + s_2) = 0.3$  units per cm. As the  $b$  axis has been placed 24 cm. from the left-hand  $a$  axis, the Q axis is 20 cm. from the latter axis and 4 cm. from the  $b$  axis. The position of the zero point of the Q scale (not that of the arbitrary cm. scale actually plotted) is readily found from the corresponding sets of values ( $a = 0$ ,  $b = 17$ ,  $Q = 4$ ) and ( $a = 6$ ,  $b = 7$ ,  $Q = 15.11$ ). Thus a straight line joining 6 on the left-hand  $a$  axis with 17 on the  $b$  axis will cut the Q axis at  $Q = 4$ , and similarly a straight line joining 6 on the  $a$  axis with 7 on the  $b$  axis will cut the Q axis at  $Q = 15.11$ .

Table for checking graph of percentage of conversion.

$a$	$b$	C	$a$	$b$	C
6	9.42	30	1	16.25	70
4.15	13	30	2.74	8	70
5	9.58	40	1	13.78	80
4.82	10	40	1.25	12	80
3	12.67	50	0.3	16.61	90
3.96	10	50	0.62	12	90
3	10.45	60	0.0	?	100
1.71	15	60			

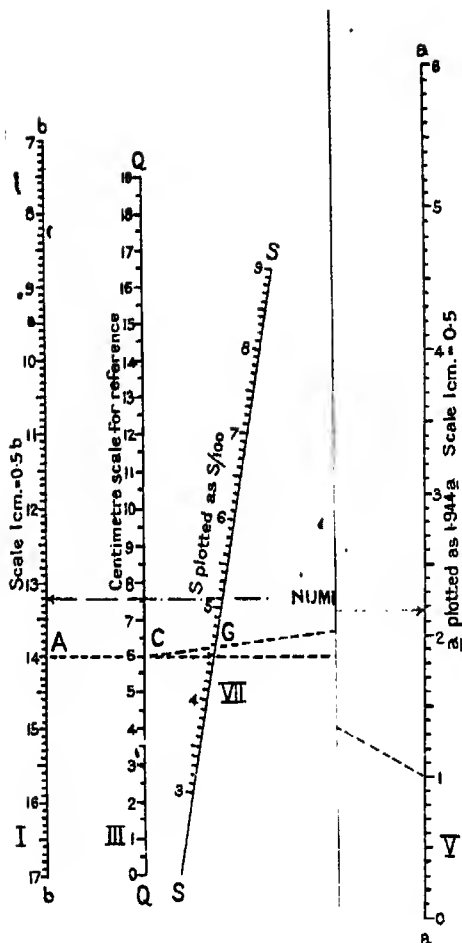
II. Percentage of  $SO_2$  in burner gas.—Equation (2) may be written in the form—

$$S/100 = Q/P$$

in which  $Q = 4.21 + 0.185a - b$

and  $P = (179.6 + 1.944a - 1.5b)$ .





The percentage of  $SO_2$  in the gaseous mixture is shown by the intersection of a stretched line DE, with that of the intersection of the scales on the vertical axis.

$S = 100 \frac{14200 + 15800T - 2(63 + 237T) - 300b}{14200 + 15800T - 2(63 + 237T) - 300b}$

in which  $S$  = Percentage by volume of  $SO_2$  in the gaseous mixture.

$a$  = Percentage by volume of  $SO_2$  in the gaseous mixture.

$b$  = Percentage by volume of  $O_2$  in the gaseous mixture.

$T$  = Volume of  $O_2$  required to produce the combustion of pyrites is shown by the intersection of the scales on the vertical axis.

The combustion of pyrites is shown by the intersection of the scales on the vertical axis.

Since the various causes of deviation from the theoretical may be taken as 1/10 or 1/375, and the percentage of  $SO_2$  in the gaseous mixture is shown by the intersection of the scales on the vertical axis.

$S = 100 \frac{14200 + 15800T - 2(63 + 237T) - 300b}{14200 + 15800T - 2(63 + 237T) - 300b}$

The graph (Fig. 10) in this case is similar in type to the previous one except that P and Q must both be found before proceeding to find S. In the numerator the scale chosen for  $a$  is 0.1 and that for  $b$  0.5 unit per cm.,  $a$  being plotted as  $0.185a$ . The scale of Q is therefore 0.6, and the distances of the Q axis from the  $a$  and  $b$  axes respectively, are to each other as 5 to 1. In the denominator  $a$  is plotted as  $1.944a$  and  $b$  as  $1.5b$ , the scale in each case being 0.5 unit per cm. The scale of P is therefore 1 unit per cm., and the P axis is midway between the  $a$  and  $b$  axes. Subject to the above conditions the relative position of the various axes is merely a matter of convenience, but, with the exception, of the S axis, they must all be parallel. The actual scales of P and Q are not required, but for convenience of reference, centimetre scales have been plotted on their axes. The S axis is part of a straight line joining the true zeros of the P and Q scales. The position of the zero of the Q scale may be found from the sets of corresponding values ( $a = 0$ ,  $b = 17$ ,  $Q = 4$ ) and ( $a = 6$ ,  $b = 7$ ,  $Q = 15.11$ ). The zero of the P axis will not be readily accessible, but its position and the slope of the S axis may be estimated as follows:—

Draw a base line through the zero of the Q axis at right angles to the P and Q axes. Find two points on the P axis from the two sets of corresponding values ( $a = 0$ ,  $b = 7$ ,  $P = 169.1$ ) and ( $a = 6$ ,  $b = 17$ ,  $P = 142.4$ ). From the position of these points relative to the intersection of the P axis with the base line the height of the zero of the P scale above the base line is readily found, and this height divided by the distance apart of the P and Q axes gives the tangent of the angle of slope of the S axis. The chief points on the non-uniform S scale may be found graphically by means of the following table. The smaller divisions must be inserted by projection from a decimal scale as previously described.

Table for checking graph of percentage of  $SO_2$ .

a	b	S	a	b	S
1	16.60	3	4	12.58	6
1	14.98	4	0	9.42	7
0	14.70	4	4	10.84	7
1	14	4.59	0	7.53	8
0	13	5	2	8.30	8
2	12.59	5	6	9.85	8
0	11.24	6			

A convenient cursor for reading these graphs is made, by ruling a line with a needle on a strip of celluloid, for example, a strip of Kodak film from which the gelatine has been removed. The line will be more distinct if it is inked over with Indian ink, the excess of ink being removed (after drying) with a slightly damp cloth. To obtain sharp readings the ruled line should face the graph.



## SECTION 2

## GRILLO OLEUM PLANT

**General outline and description of plant.**—The Grillo plant was designed for the use of sulphur as raw material instead of pyrites on account of the lesser demand made on skill in burning and also of the saving in freight. The plant, however, can be easily adapted for using pyrites by replacing the present sulphur burners by suitable burners for pyrites and slightly increasing the gas purification system.

The sulphur dioxide formed by burning sulphur in air, is passed after purification over finely divided platinum supported on granulated anhydrous magnesium sulphate and is converted into sulphur trioxide which is absorbed in sulphuric acid, and strong sulphuric acid of any desired strength or oleum up to 20 per cent. of free  $\text{SO}_3$  is produced.

The plant was built in so-called double units, each double unit capable of producing 50 tons of  $\text{SO}_3$  per day. At Queen's Ferry five double units were erected. Fig. 11 shows the general arrangement of that installation.

The sequence in which the various parts of the plant come into play and the course of the gases through the plant are as follows (see Fig. 12).

Sulphur is charged into the cast-iron burner pans and there burned to  $\text{SO}_2$ , which, mixed with 90 per cent. of air, passes from the burner to the burner flue and heater cooler in succession. The latter serves as a dust chamber; this is not an important function when burning a comparatively pure raw material such as sulphur, although it is of primary importance when burning pyrites or blende. The gases then pass to the  $\text{SO}_2$  coolers, where they are cooled to atmospheric temperature. In the sulphur burners some  $\text{SO}_2$  is converted to  $\text{SO}_3$ , usually about 2.5 per cent. of the total; this combines with the water in the gases, undried air being used to burn the sulphur, and along with undeposited dust forms sulphuric acid and sulphuric acid mist, 10 per cent. of this is condensed in the  $\text{SO}_2$  coolers as  $\text{H}_2\text{SO}_4$  of 65 per cent. strength. From the latter the gases pass to Nos. 1 and 2 filters in succession, these take out 40 per cent. of the mist, referred to above, as  $\text{H}_2\text{SO}_4$  of 55-60 per cent. strength. Then follow three sulphuric acid drying towers and three more filters. On leaving the last of these, the gases should be optically free from mist or fog. They then enter the pressure equaliser and the blower; the former, by an arrangement of baffle plates, absorbs the pulsations of the latter and prevents the vibration being carried to the lead filters, the blower provides the driving force for the plant; up to this the latter is under suction and from this point onwards is under pressure.

Following the blower is another coke filter, the object of which is to catch any grease or residual mist in the gases. These then enter the heat exchangers where they are heated by the hot gases from the converters. Afterwards they pass backwards again, to the heater cooler, this time being inside the tubes, which are heated by the gases





direct from the burners. They should here receive enough heat to enable them to reach the converters, hot enough to start the reaction  $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ , but should this not be the case they are passed through the preheaters, which are the ordinary type of fire heated tubes, before going into the converters. After leaving the latter the gases go through the heat-exchangers, this time outside the tubes, the  $\text{SO}_3$  coolers, the absorption towers and into the atmosphere. The absorbing acid and oleum go through coolers, circulating tanks, stock tanks, and then to storage. Feed acid is added just as the absorbing acid leaves the towers and before entering the coolers.

**Raw material.**—Sulphur from Louisiana, Sicily and Japan was used. It is important that the sulphur be free from arsenic, selenium, and the halogens, or else that these impurities be not present in larger amount than can be safely treated in the purification system of the plant.

As it is required to run the plant regeneratively, however, that is, without the use of fuel for heating up the gases, it is necessary to have a fairly pure sulphur in order to obtain sufficiently high temperature to heat up the gases to the proper degree before entering the conversion vessels.

The analysis of an average sample of sulphur is as follows :—

	Per cent.
Sulphur (by difference) - - - - -	98.950
Moisture - - - - -	0.410
Sodium chloride - - - - -	0.002
Ash - - - - -	0.310
Insoluble in chloroform (other than ash) - - - - -	0.320
Arsenic - - - - -	—
Selenium - - - - -	—
	<hr/> 100.000 <hr/>

The only dangerous constituent in the above is sodium chloride; the quantity is, however, small, and when this is decomposed in the burners to  $\text{HCl}$  and  $\text{Cl}_2$  the purification plant is quite capable of washing it out, the working limit of sodium chloride in the sulphur is 0.02 per cent.

Practically all the sulphur is burned off in the burners, and there is no loss from this source, the ash residue usually contains—

	Per cent.
Sulphur - - - - -	0.001
Sodium chloride - - - - -	0.002

As the ash is only 0.8 per cent. of the total it is obvious that almost the whole of the sodium chloride is decomposed also.

**Varieties of acid produced.**—Generally acid containing 98 per cent.  $\text{H}_2\text{SO}_4$ , and oleum containing 20 per cent. free  $\text{SO}_3$  were produced.

In the former case the sulphur trioxide is absorbed by 98 per cent.  $\text{H}_2\text{SO}_4$ , which is pumped continuously to the tops of the towers and distributed over the quartz. The acid as it flows down the towers dissolves the sulphur trioxide from the ascending gases and increases in strength. After reaching about 100 per cent.  $\text{H}_2\text{SO}_4$  it is reduced in strength to 98 per cent. again by the addition of water or weak sulphuric acid, cooled and pumped over the towers again. As the quantity of acid is continually increasing, a regular quantity of 98 per cent. acid is pumped away for use or storage. The greater part of the sulphur trioxide is absorbed in the first tower of the series, the second and third acting as wash towers. Acid containing 98 per cent.  $\text{H}_2\text{SO}_4$  is used for absorption because sulphur trioxide is most soluble in sulphuric acid of this strength.

When oleum, which is a solution of  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$  is required, the first tower is used for this purpose, the second and third acting as wash towers as before, the acid running from the first tower must therefore be isolated from the acid from the other two. Part of the acid from the second and third towers is allowed to gravitate from the first circulating tank to the second and from the second into the third at the base of the oleum tower; in this tank it meets oleum containing about 26 per cent. free  $\text{SO}_3$  which is running in from the oleum tower, the two mix with the 20 per cent. oleum already in the tank to make more 20 per cent. oleum. Part of this runs in a constant stream to storage and represents the make. This run-off is also the cause of the gravitation from the first two tanks.

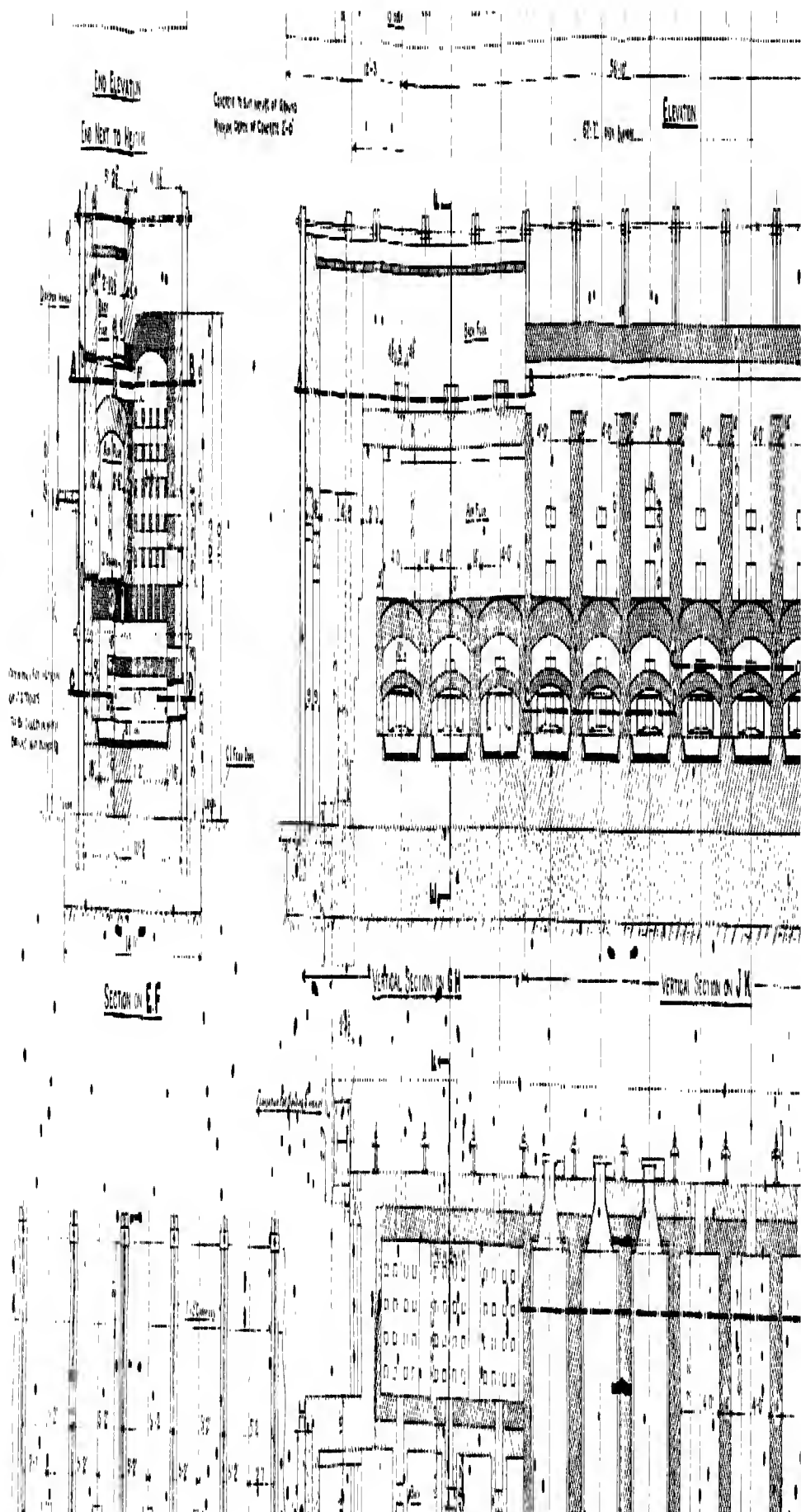
#### DESCRIPTION OF THE PLANT

For convenience of description one unit may be divided into the following sections:—

- |                            |                                  |
|----------------------------|----------------------------------|
| 1. Sulphur store.          | 9. Grease catcher.               |
| 2. Sulphur burners.        | 10. Heat exchanger.              |
| 3. Heat cooler.            | 11. Heater cooler (inner tubes). |
| 4. Sulphur dioxide cooler. | 12. Preheater.                   |
| 5. Coke filters.           | 13. Converter.                   |
| 6. Scrubbers.              | 14. Sulphur trioxide cooler.     |
| 7. Suction equaliser.      | 15. Absorption house.            |
| 8. Blower.                 | 16. Storage tanks.               |

(1) **Sulphur stores.**—Sulphur is conveyed in railway trucks from the docks to the sulphur stores; it is there discharged by hand on to an iron grid with bars 4 inches apart, this is to prevent large pieces getting through, the fall of the sulphur on to the grid is sufficient to break the larger pieces, all go through on to an endless rubber belt conveyer which carries the sulphur to an elevator, the latter deliver it to another rubber belt conveyer and from this the sulphur can be tipped into any part of the store; this is built of steel and corrugated iron with a concrete floor, and can be of any dimensions; the sides are built at the angle of repose for greater economy; bogey tracks are laid





at convenient distances, trolleys are brought in, containing empty scoops, these are loaded with a known weight of sulphur, and wheeled back to the sulphur burners.

(2) **Sulphur burners (Fig. 13).**—Each unit has one battery of 12 burners, each capable of burning 90 lb. of sulphur per hour.

The burners are cast-iron pans 7 feet by 3 feet, 6 inches by  $\frac{3}{4}$  inches deep, which are set in brickwork and have a charging door at the front containing an air slide for regulating the amount of air drawn in. Two arches of fireproof bricks are built over each pan and above the upper arch a short vertical flue of chequered brickwork which runs into the main horizontal flue into which all the separate burners discharge.

A charge of sulphur is generally about 75 lb.; each scoop contains half a charge; two scoops are charged to each burner per hour, so with 12 burners 900 lb. of sulphur are charged per unit per hour.

The sulphur melts in the hot pan and partly burns and volatilises; the sulphur dioxide gas and sulphur vapour pass to the rear of the pan under the lower arch then rise to the upper arch, pass under it and rise through openings at the top into the chequered brick chamber and then enter the main flue connected with all the burners and return through a back flue on the same level to the heater cooler.

Secondary air for the combustion of sulphur vapours enters from the hot air flue before the gases pass into the chequer work.

The burners are lagged to conserve as much heat as possible.

The pans and burners work very efficiently and retain their heat for several days. The plant can be shut down for five days and still leave the burners sufficiently hot to re-start burning the sulphur. In order to have a regular percentage of sulphur dioxide in the gas, which is necessary to secure good conversion, it is essential that the charging of the burners be systematically performed.

**Sublimation.**—When the burners are charged at the rate of 75 lb. per hour with sulphur containing up to 2.0 per cent. ash, it is usual to clean them every three or four days. This is done by merely opening the burner door, after the charge has burnt off, and raking out the ash into a barrow placed beneath, each burner is done in turn, the time required for each one being about five minutes, *i.e.*, 60 minutes for the unit.

When the ash is completely removed the sulphur burns away very quickly and tends to give irregular percentages of  $\text{SO}_2$ , this is corrected by only partially cleaning the pans, *i.e.*, by leaving a thin layer of ash on the bottom to insulate it and so slow down the rate of combustion.

Recently an attempt was made to reduce the inconvenience of burner cleaning by allowing the ash to accumulate until the pans were quite full, *viz.*, for 20-30 days; by this means very regular burning was obtained, but after about eight weeks the percentage conversion began to decrease, for various reasons the above practice might have been responsible and a return was made to the older method. An attempt was made later to prove whether or not the decreased conversion was due to the accumulation of ash. This consisted in selecting a unit with very high conversion, and allowing the ash to remain as before. No



H.M. FACTORY QUEEN'S FERRY - GRILLO PLANT.  
 SHEWING ARRANGEMENT OF BAFFLE WALLS IN HEATER-COOLER.

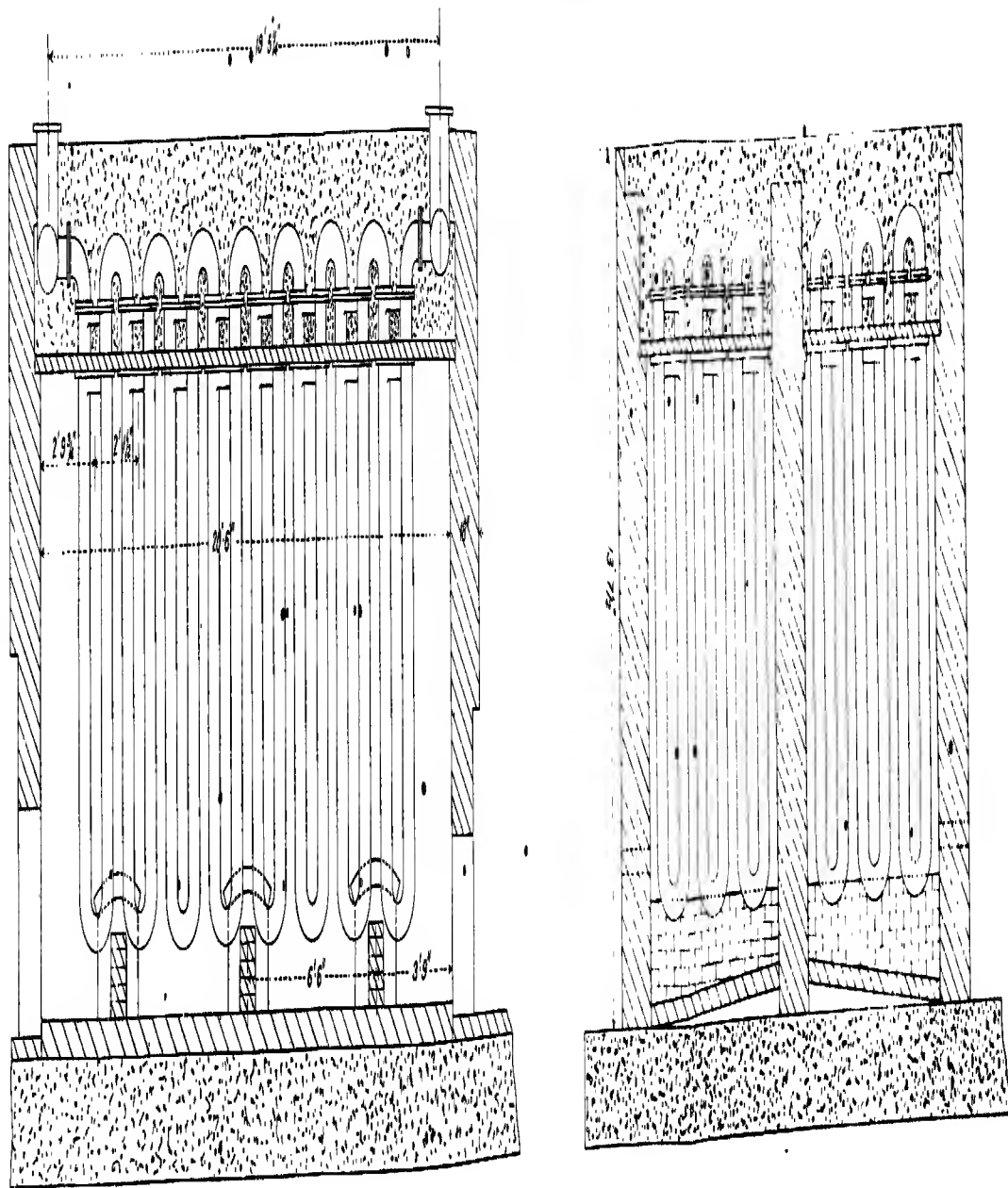
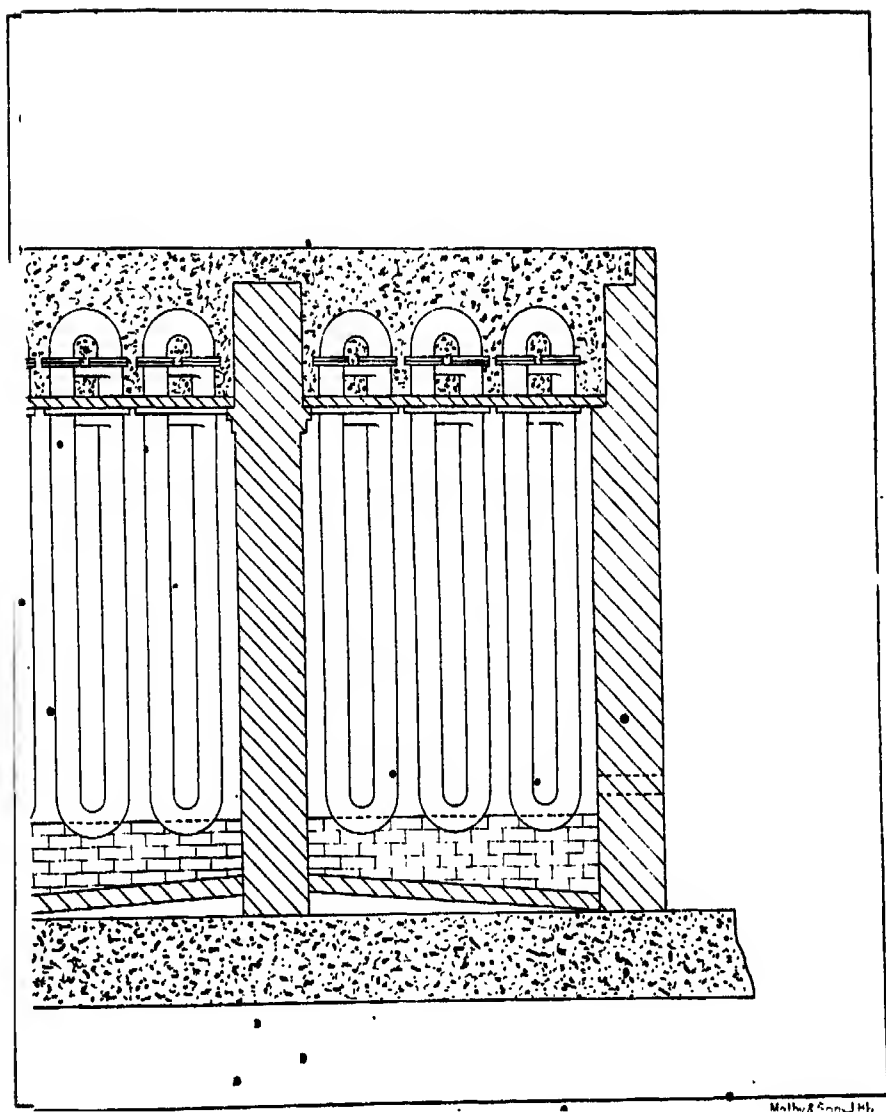
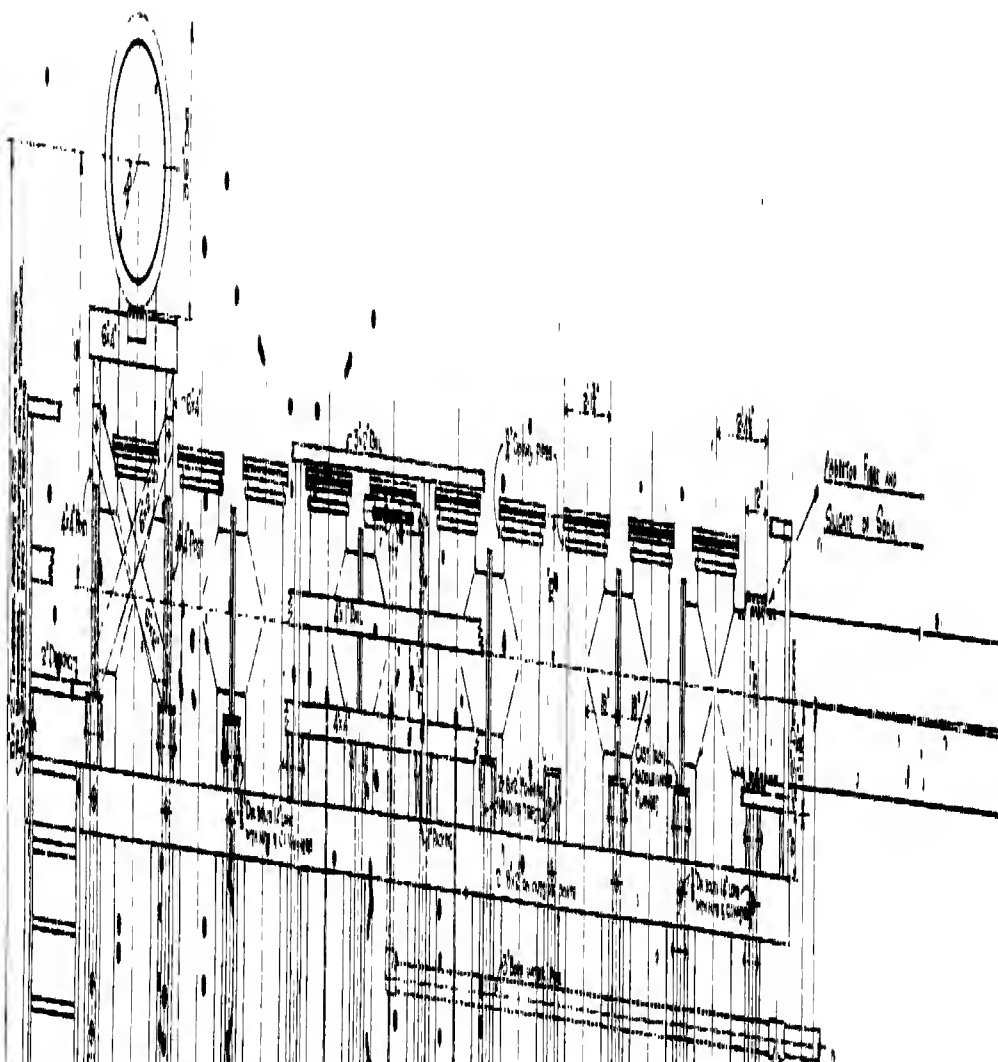
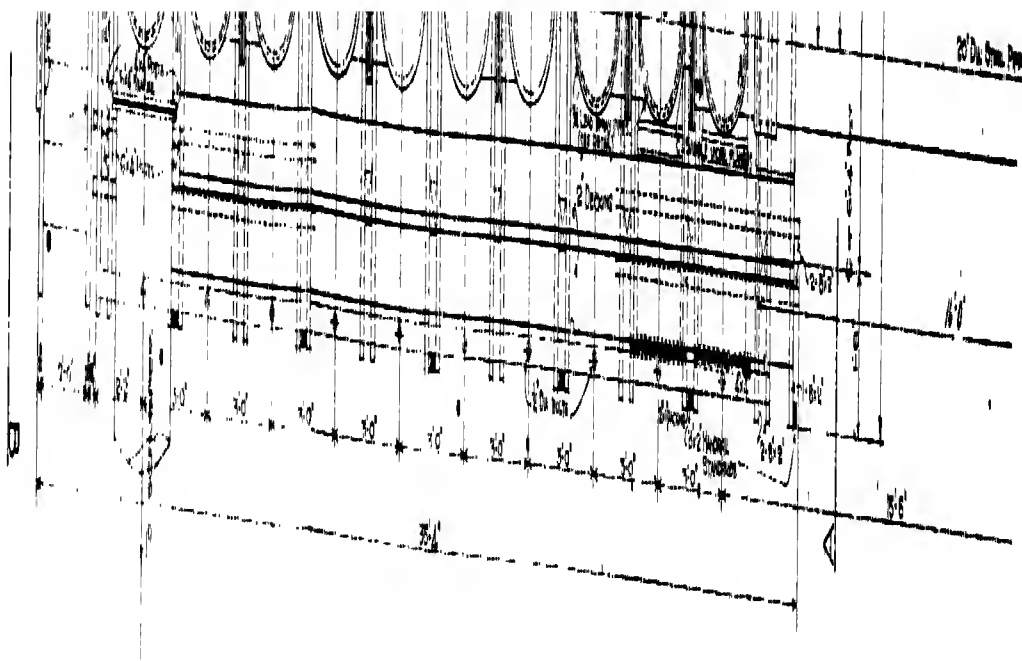


FIG. 14





(3) ~~Heater-cooler or dust chamber~~.—The functions of this part of the plant are—

- (a) To cool down the hot gases from the burners;
- (b) To heat the cooled purified gases previous to conversion;
- (c) To collect the dust carried forward by the burner gases.

This is a brick chamber 23 feet 6 inches long by 18 feet wide by 10 feet high, divided longitudinally into two separate compartments by an 18 inch wall. Each compartment contains three rows of eight U pipes, 5 inch internal diam. round which the hot impure gases circulate before being led away to the  $\text{SO}_2$  coolers. Purified gases pass through the U pipes in the heater cooler on their way to the converter, and receive heat from the hot impure gases which require cooling before purification.

Each compartment is connected to the burner flue, and the impure gases leave by a brick flue which has two up-takes, one for each set of  $\text{SO}_2$  coolers. At one factory it was considered that the cross-sectional area of the pipes was too small and should be increased.

The chamber is insulated by cavity walls, the cavity being filled loosely with slag wool. Stagnant dust pools, to prevent the fine dust from being caught up again in the current, were made by building 9 inch wall, 18 inches high, at right angles to the direction of the current.

The impure gases leave the dust chamber and enter the coolers at about  $290^\circ \text{C}$ .

Fig. 14 gives a side and end elevation, showing the two compartments, the low wall forming the dust pools, and the U pipes.

(4) Sulphur dioxide coolers (Fig. 15).—These coolers consist of two series of 20 vertical lead cylinders, 20 inches diameter by 13 feet 6 inches high, the bottom bends are supported on carved wooden blocks fixed inside a trough which is permanently filled with running water. This water is sprayed uniformly round the first four cylinders at the top in each series, runs into the trough and then away to the drain. Care must be taken to keep the water continually sprayed on to these cylinders, otherwise the lead would soften and collapse; this once partially occurred owing to water ceasing to flow through the main.

The hot gases entering the cooler pass downwards through the first header into the bottom of the second header, up the pipe, across the branch connection at the top, and down the next header, and so through the whole series of 20 pipes. The cooled gases finally pass from the top of the last pipe into a 30 inch diameter lead delivery main leading into the first filter.

The duties of these coolers are—

- (a) To cool the gases down to atmospheric temperature;
- (b) To condense as much acid mist as possible.

Each header is supplied at the side with a blanked flange top and bottom, which can be easily removed and the headers cleaned by means of a hosepipe. At the bottom of each cylinder a lead drain pipe, 1 inch diameter, leads to a leaden catch-pot, the outlet of which delivers the

condensate to a  $1\frac{1}{2}$  inch lead pipe running along each side of the cooler and carrying condensed acid to a small Pohle lift, which removes it for concentration.

On the last header of each system an opening, 9 inches by 6 inches provided with a sliding cover, is used for admitting air to dilute the gas from between 10 and 12, to 5 per cent. of  $\text{SO}_2$ , which is the best concentration. About 10 per cent. of the mist and sulphuric formed in the burners is deposited in the coolers as 70 per cent.  $\text{H}_2\text{SO}_4$ .

(5) **Coke filters (Figs. 16 and 17).**—There are five rectangular boxes, 30 by 12 by 10 feet, made of 8 lb. lead, lined with acid proof tiles, and filled with graded coke laid on a brick grid. The specification for coke-filling is as follows :—

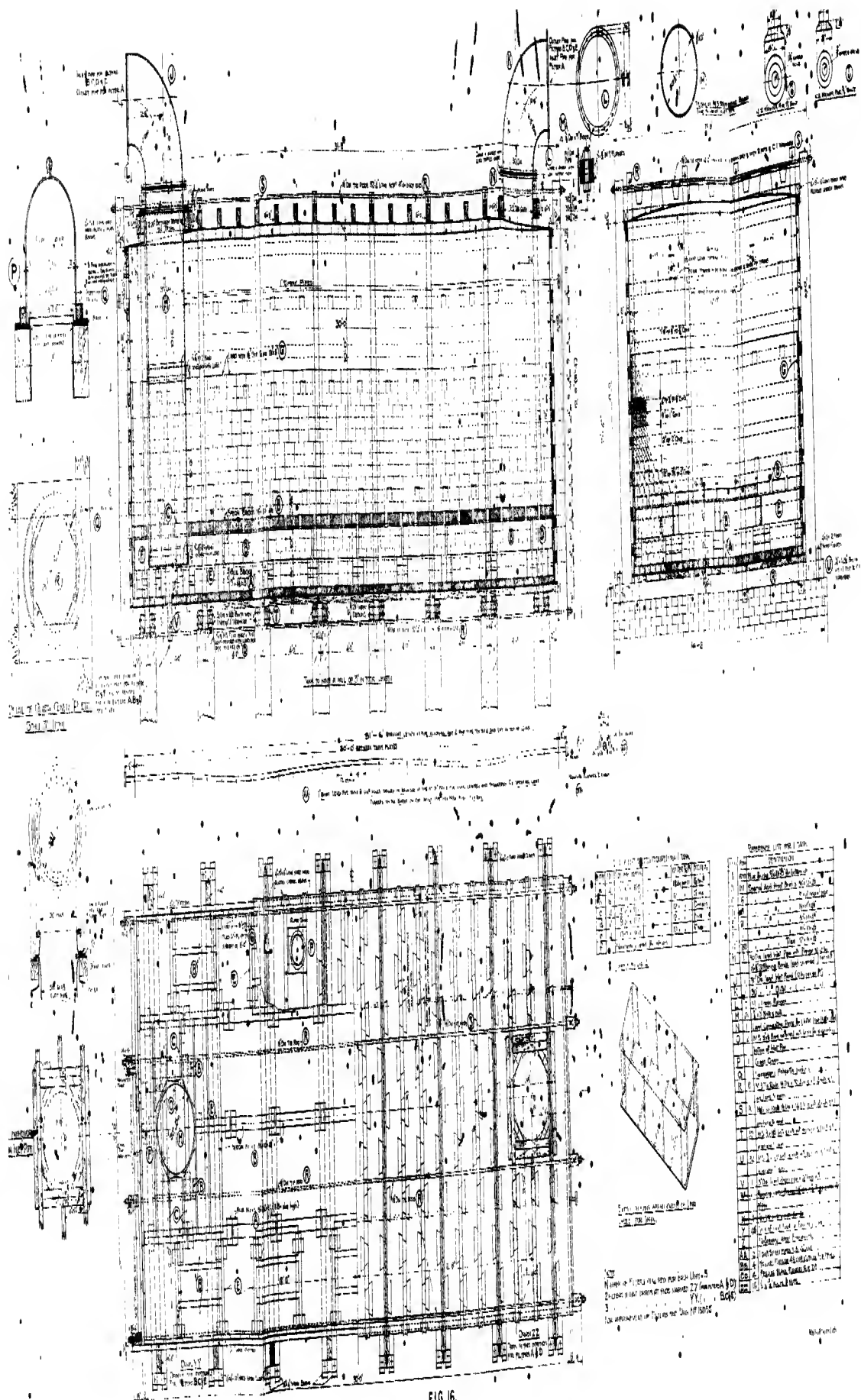
24 inches of 4 inch to 6 inch coke.  
 12 inches of 4 inch coke.  
 12 inches of 2 inch coke.  
 4 inches of 1 inch coke.  
 48 inches of  $\frac{1}{8}$  to  $\frac{1}{16}$  inch coke.  
 20 inches of free space.

In the 20 inch space over the coke-filling, two 1 inch lead pipes, perforated on the under side with  $\frac{1}{8}$  inch holes are fixed in order to flush the filter with acid for removing moisture or for freeing the filter from frozen acid when occasion arises. A hole, 12 inches diameter, is cut in the top of the filter and is provided with a glass cover easily removable for the purpose of observing the nature of the gas in the filter.

The filters are fixed on brick piers 5 feet high to allow the sulphuric acid which condenses in them to run first into a collecting launder and then into a small tank with pump attached. The gases from the  $\text{SO}_2$  cooler pass into the top of the first filter and down through the coke and issue from the bottom, whence they are conducted through a wide lead pipe, 30 inches diameter, to the top of the second filter, and from it to the first scrubbing tower. These two filters are very efficient, and condense 40 per cent. of the acid and mist formed in the burners; this runs out through a lute into the launder in a steady stream of 60 per cent.  $\text{H}_2\text{SO}_4$ . The coke is always wetted by the condensation of this acid. Any sublimed sulphur which has escaped oxidation is deposited on top of the coke in the filter and can be removed when necessary.

(6) **Scrubbing towers (Figs. 17 and 18).**—Three in number, 12 feet square and 27 feet high, are built of 8 lb. lead supported on wooden framework. The inside is lined with acid proof tiles and filled with graded coke as in the filters, except that the smallest size is 1 inch. The lead casing extends to within 3 inches of the 16 lb. lead sancer at the base, on which the grid carrying the filling stands, and is left free to allow for any "creeping" of the lead. The brick chequer work at the bottom is so constructed that the gases entering the bottom of the towers pass along the central channel and then through the chequer









# GRILLO OLEUM PLANT.

## SCRUBBING TOWERS.

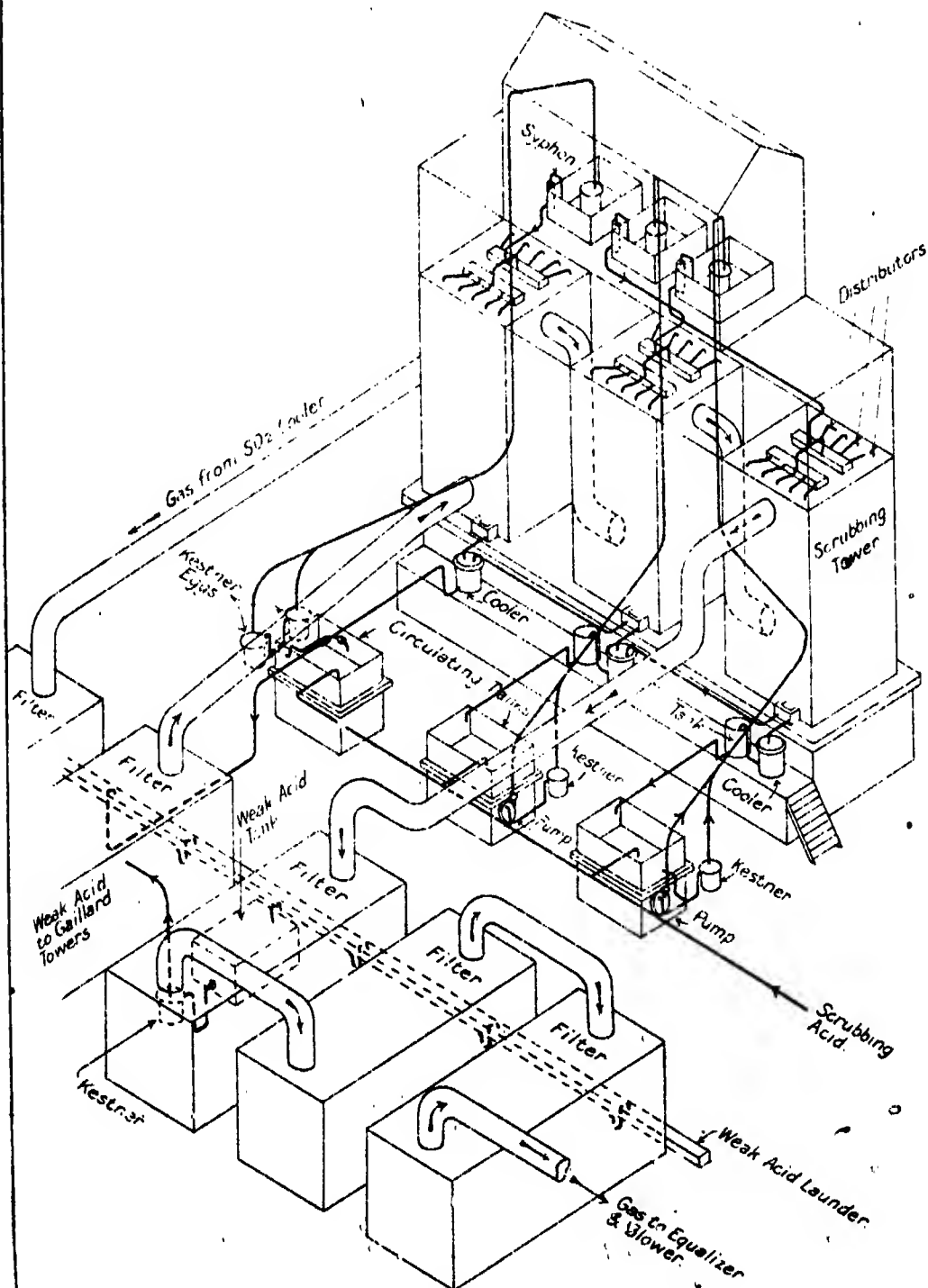


FIG. 17.

brickwork into the side compartments, thus giving an even distribution of gas over the whole cross-section.

The towers stand on a concrete base supported on piles sufficiently high to allow the acid to flow from the bottom of the towers into a receiving tank, whence it is pumped to another lead-lined wooden tank placed above the top of the tower.

Distributors split up the feed acid over each tower into 72 equal streams conveyed by  $\frac{3}{4}$  inch lead pipes to each of the lutes in the top section. Above this are arranged three feed tanks, each 7 feet long by 4 feet 6 inches wide by 3 feet 6 inches deep, lined with lead.

On the ground level, in front of the scrubbing towers, are the lead-lined feed tanks, one for each tower, measuring 10 feet by 6 feet 6 inches by 3 feet 6 inches.

The scrubbing towers are numbered 1, 2 and 3, according to the passage of the gas. Strong sulphuric acid, about 96 per cent., is run into the tank at the foot of No. 3 tower, and is elevated by means of a centrifugal pump to the feed tank in the house at the top of the scrubber. This acid, for drying purposes, leaves the feed tank by  $1\frac{1}{2}$  inch lead pipe, the latter splitting up into two 1 inch lead branch pipes which lead to the centre of the two distributors. Flow is controlled by regulus valves. From here the acid is distributed through the lutes and percolates through the coke filling of the tower, finally running out through a lead cooler at the bottom into the above-mentioned feed tank on the ground level. A 3 inch lead pipe forms an additional outlet for acid from the saucer of the tower into the feed tank. Acid from the saucer of No. 3 tower can be bye-passed through a 3 inch lead pipe controlled by a valve into No. 2 feed tank, from whence, as in the case above mentioned, the acid is elevated to the feed tank at the top of No. 2 tower. Similarly, acid can be bye-passed from the saucer of No. 2 tower into No. 1 feed tank, and thence to the top of No. 1 tower. Acid from the saucer of No. 1 tower can, if necessary, be bye-passed to the lead box which collects all weak acid to be sent for concentration. At one plant the acid in the three feed tanks is roughly of the following strengths :—

							Per cent.
No. 3	-	-	-	-	-	-	95
No. 2	-	-	-	-	-	-	90
No. 1	-	-	-	-	-	-	70

Acid under 70 per cent. is removed for concentration.

Elevation of acid from the bottom feed tanks is by means of 10 inch impeller Rees Roturbo pumps, directly coupled to 4 h.p. motors. The delivery pipe is  $1\frac{1}{2}$  inch lead piping. Kestner automatic elevators are installed to act as spares when the centrifugal pumps are out of action. The pumps can elevate 10 tons of acid per hour to each scrubber—height of lift, 53 feet.

The gas passing through the three scrubbing towers in series leaves No. 3 tower and enters the bottom of No. 3 filter, and thence through 4 and 5 filters. Leaving No. 5 filter, the piping changes to 30 inch

diameter mild steel pipe. Along this pipe the gas flows to the suction equaliser. The distance between the centres from No. 5 filter outlet to the equaliser is 71 feet.

The function of these towers is to remove halogens, mist and moisture.

The scrubber acid for No. 3 tower is kept up to strength by adding pure oleum (oleum made with water feed) from the storage tanks. No. 2 can also be strengthened by adding oleum direct, or by passing some of the acid leaving No. 3 scrubber into the tank feeding No. 2. No. 1 scrubber is kept up to strength by passing acid from No. 2 scrubber to the feed tank for No. 1. As the bulk of the acid increases, acid is withdrawn from No. 1 feed tank and sent to the concentration plant. Specific gravities and temperatures of the acid in each reservoir are taken once each shift. Only small quantities of the stronger acid, about 3-4 inches, are added at one time in order to avoid serious rise in temperature.

Temperature rises to about 40° C. after addition of 5 inches of oleum (or 3,210 lb.). It has been noticed that as a result of adding 10 to 12 inches of oleum fairly rapidly to No. 2 feed tank the converter temperatures were upset. The presence of chlorine has been detected under these conditions, and it seems quite reasonable to assume that the trouble was due to increase of concentration and increase of temperature, both factors which would render hydrochloric acid less soluble in the scrubber acid. From the scrubber the gases pass through the remaining three coke filters, but now enter at the bottom, and pass out at the top of each filter in succession. The object of these filters is to retain any residual mist or acid spray still left in the gases or carried over from the towers. The gases leaving No. 5 filter should be optically clear. It is essential that the coke used in these filters should contain not more than 1 per cent. of moisture when put in. Relatively wet coke has been used for filling filters and an attempt made to dry it by spraying with strong sulphuric acid, but this was not effective, the initial moisture made the gas misty.

The acid discharging from the filters is generally 85 per cent.  $\text{H}_2\text{SO}_4$ ; this freezes at  $+4^\circ\text{C}$ .; in winter this sometimes becomes solid and blocks the filters; the frozen acid is melted by spraying with 94 per cent.  $\text{H}_2\text{SO}_4$ , the sprays are installed in the filters as a fixture, and are connected to the strong acid tank over No. 3 tower so that by turning the valve a spray of strong sulphuric acid is at once put over the coke; the effect is instantaneous, the frozen acid melting at once.

(7) **Suction-presser equaliser.**—This consists of a mild steel cylindrical shell of 5 feet diameter by 6 feet deep and of  $\frac{1}{4}$  inch steel plate. Inside the shell are fixed two, and in some cases three, steel diaphragm plates made of  $\frac{1}{4}$  inch mild steel, and perforated all over with  $\frac{1}{4}$  inch diameter holes spaced at  $\frac{3}{4}$  inch centres. The diaphragms are placed, one at the bottom, one in the middle, and if there is a third, one at the top. The top and bottom covers of this cylindrical shell are cast-iron, and of conical shape. The top cover is connected to the last filter by

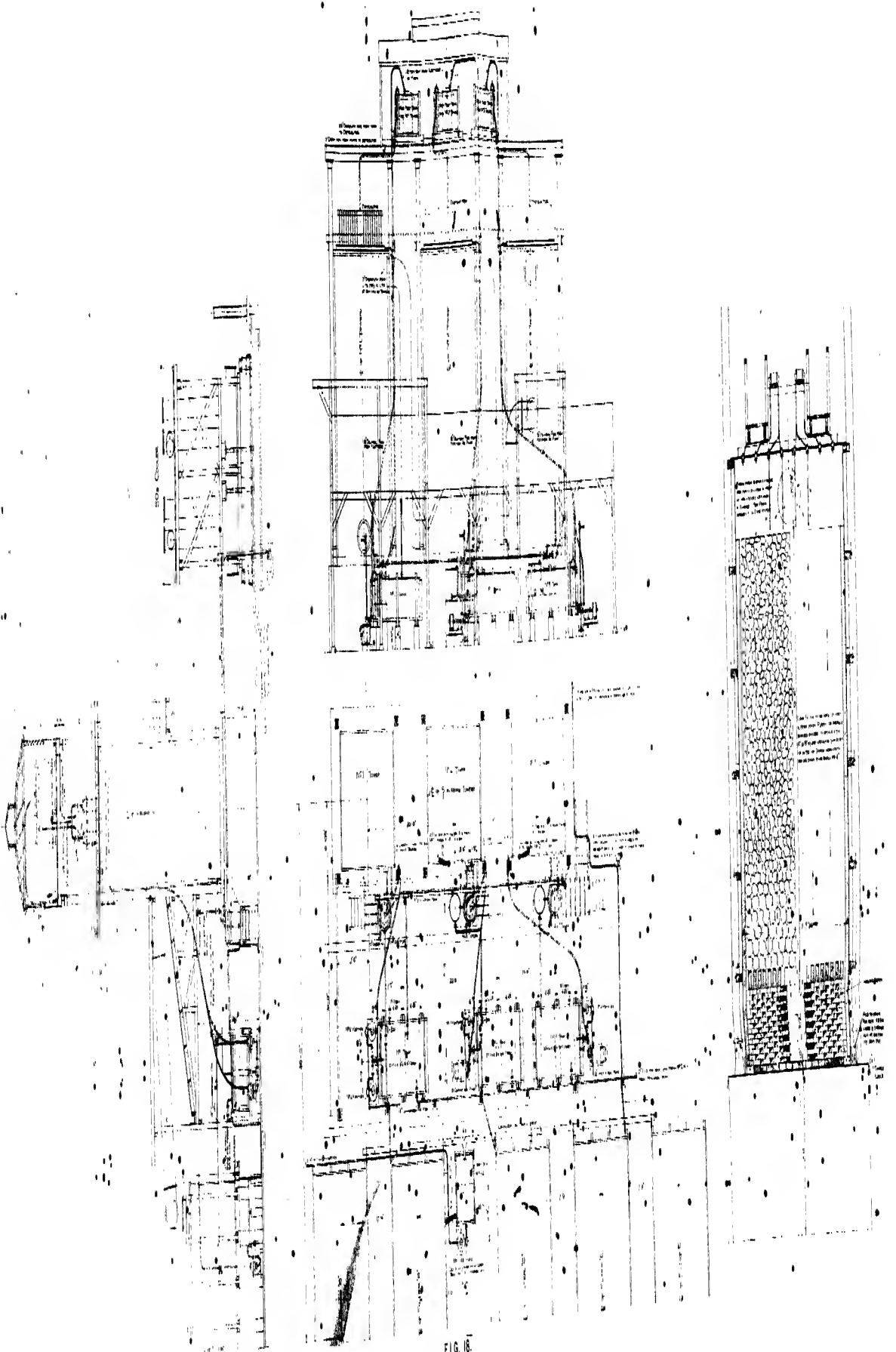


FIG. 18.



means of the 30 inch diameter mild steel pipe referred to above, whilst the bottom cover is fitted with a 30 inch to 16 inch cast-iron reducing pipe, which connects by a 16 inch suction pipe to the blower.

The function of the equaliser is to neutralise the marked tendency of the blower to develop pulsations in the suction pipe which would have a serious effect on the lead covers of the filters causing them to vibrate in sympathy with the blowers, and the lead to crystallise and crack. In one of the plants it was found advantageous to cover three-quarters of the holes with a sheet of 12 lb. lead, and the uncovered portions were staggered. Instead of a rigid joint connecting the 30 inch lead bend and the filters a luted pipe was substituted in some units and proved a great success, doing away with the repairs frequently necessary owing to the cracking of the flanges caused by the vibration.

As this condensate from the equaliser is about 86-88 per cent. acid, much trouble was experienced during cold weather owing to freezing of this acid on the diaphragms. In order to overcome this, hot gas can now be led into the top of the equaliser from the pipe leading from the heater cooler to the preheater or converter. This bye-pass is a 3 inch pipe, and the supply of gas for it is regulated by a valve in the converter house. This has proved very efficient in practice. The gas now enters the blower.

(8) **Blower.**—This is of the Roots' design, and has a capacity of 29 c.f. per revolution. The drive is by a 12 inch diameter belt from the pulley of a 60 h.p. motor, giving 158 r.p.m. to the blower. The glands of the blowers are packed with white asbestos cord boiled in mineral jelly for 24 hours. This method of treatment has given satisfactory results. Previous to this, lantern rings and compressed air were used in addition to the packing. The delivery pipe from the blower is of 18 inch diameter, and leads to the grease catcher. A 10 inch diameter pipe connects the suction to the pressure side of the blower. A gate valve in this pipe controls the flow of gas, and so enables one to regulate the suction and corresponding pressure of the blower.

(9) **Grease-catcher.**—This consists of a 30 feet by 8 feet cylinder of mild steel. At the bottom inside this tank rests a cast-iron grid constructed of special cast-iron firebars. These bars are so arranged as to give a  $2\frac{1}{2}$  inch clear space between their underside and the inside bottom of the tank. At each end of the tank, and at point 3 feet 3 inches above the centre line of the vessel, is provided a fitting which receives a sight glass, so that an optical test can be made at any time, a light is fixed at one end for night observations.

At the bottom of the tank and at the end furthest away from the inlet pipe, a run-off drain pipe is fitted. This is provided with a lute of sufficient depth to counter-balance the maximum pressure which will be reached at any time.

Through the 16 inch fitting at one extremity of the grease catcher, a 15 inch gas main is taken downwards through the coke with which the vessel is packed to a point just below the cast-iron grid upon which the graded coke rests. Through this, gases from the blower enter and

rise upwards through the coke filling before they escape through the outlet fitting at the opposite end of the tank. Grease catcher is a misnomer, it is supposed to trap grease and oil from the blower, but is actually the means of trapping acid mist, and also functions as an equaliser on the pressure side of the blower.

From the grease catcher a 15 inch diameter steel pipe runs along the back of the converter house; this pipe being provided with two 10 inch diameter branch pipes connected to the inner tubes of the heat exchanger, each branch being fitted with a 10 inch cast steel fullway gate valve to control the flow of gas and ensure equal distribution to each exchanger.

*Purification.*—The purification of  $\text{SO}_2$  obtained from arsenic-free sulphur, practically resolves itself into what has come to be called the "mist question." The following are facts:—

(1) Coarse coke is practically useless for the elimination of mist.

(2) Fine coke, *i.e.*, coke passing the  $\frac{1}{8}$  inch mesh sieve, is a very efficient mist catcher, but a considerable depth is necessary, certainly more than 1 foot in each filter and probably 3 feet or 4 feet.

(3) When the  $\text{SO}_2$  at the burner flue is 10.0 per cent., and no more air is admitted until the main entering the second scrubbing tower is reached and the gas is there diluted to 5.0 per cent.  $\text{SO}_2$ , the quantity of mist eliminated in the purification system is far greater than under any other condition tried on this plant. This practice when introduced at Queen's Ferry, solved the "mist question."

(4) Variation in the velocity of the gas up to the degree of halving it does not produce any visible difference in the amount of mist deposited.

The strength of the scrubbing tower acids are:—

					Per cent.
Strong acid	-	-	-	-	93-95
Middle acid	-	-	-	-	75-85
Weak acid	-	-	-	-	55-60

The weak scrubber acid is kept as near to 55 per cent. as possible, to take up any halogen present in the gases. A suitable quantity of weak acid is run off each day and 30 cubic feet of fresh acid from the middle tower added to prevent it becoming saturated. In order to maintain the weak acid at this strength it is necessary to add 600 lb. of water to it daily.

When the strong acid is kept at 93 per cent. to 95 per cent. the middle acid strength adjusts itself and the weak is brought down to 55 per cent. by the addition of water.

The pressure equaliser acts as a mist catcher and deposits from 20-50 lb. daily, according to the humidity and the temperature of the atmosphere.





H. M. FACTORY QUEEN'S FERRY.  
 SHEWING HEAT EXCHANGER IN USE AT GRILLO OLÉUM PLANT.

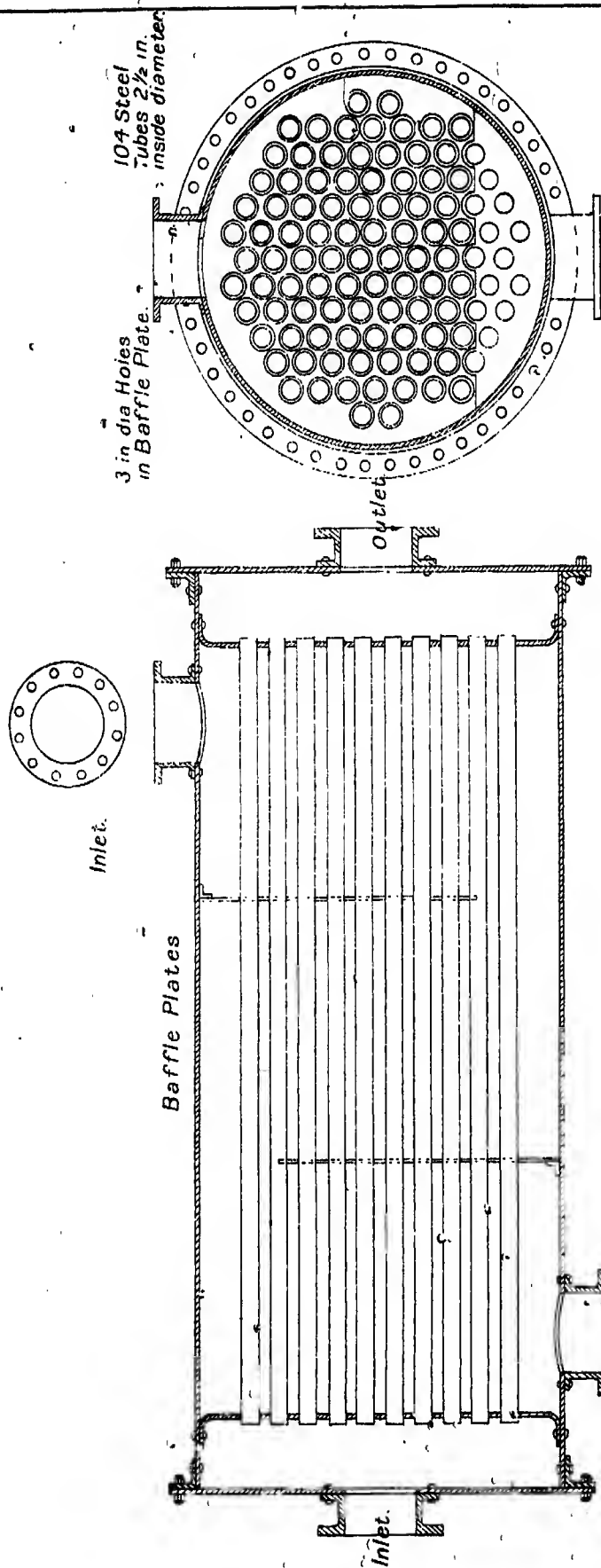


FIG. 19.

Scale  $\frac{3}{16}$  in. = 1 ft.

A slight drip, about 10 ozs. daily, is obtained from the gas main leaving the grease catcher.

TABLE

No. of Exp.	Strength of Mist as per cent. $H_2SO_4$ .	Quantity of Mist lb. per day.	Quantity of Mist grms. per 100 litres.	Sulphur charge lb.	Condition Unit 10.
2	47.1	135.0	0.07	50	Air admitted at $SO_2$ coolers.
3	30.8	111.0	0.04	70	Filters 3 and 4 sprayed every 12 hours.
4	31.6	186.0	0.12	40	Double quantity of acid over scrubbers.
5	31.6	418.0	0.15	70	Double quantity of acid over scrubbers. $SO_2$ added to burner flue.
7	24.7	294.6	0.10	75	Normal.
8	47.3	189.0	0.07	70	Normal.
9	48.0	334.0	0.12	70	$SO_2$ added to burner flue.
10	61.2	201.2	0.09	70	6 per cent. $SO_2$ at converters.
11	96.4	58.8	0.02	80	Secondary air added between 1st and 2nd scrubbers.

• (10) Heat-exchanger (Figs. 19 and 20).—This consists of a mild steel cylindrical shell 10 feet long by 4 feet 2 inches internal diameter with plate thickness of  $\frac{3}{4}$  inch. Inside the cylindrical shell are riveted two  $\frac{9}{16}$  inch tube plates, the space between the tube plate and the end plate being  $\frac{9}{16}$  inches at each end, each plate being drilled to receive 104 steel tubes  $2\frac{1}{2}$  inches internal diameter by  $10\frac{3}{8}$  W.G. thick. Between the tube plates in the cylindrical shell are placed two  $\frac{1}{2}$  inch baffle plates to force the gas passing round the tubes to take a zigzag course instead of passing across the space between the inlet and outlet openings. Through the tubes the cold purified gases flow to receive heat at the expense of hot gases from the converter, which flow around the inner tubes and which require cooling before absorption. Each unit is provided with two heat-exchangers. The two outlets from the tube spaces are connected into a 10 inch diameter main running along the inside of the house. These two 10 inch mains lead into a 15 inch main which passes across to the heater cooler, one end of the main being connected to the inner tubes of the heater cooler.

The heat exchangers are similar in principle to a water-tube boiler, they are steel cylindrical vessels 10 feet by 4 feet containing 100  $2\frac{1}{2}$  inch tubes; the latter are sweated into a plate at each end, in addition there are end plates. The spaces between the plates at each end serve as headers for distributing the gases among the tubes. Cold gases enter at one end and leave at the other after being heated to about  $100^\circ C$ . by the gases from the converters, these enter at  $400^\circ C$ . and pass on the outside of the tubes. There are two baffle plates inside to make the latter gases take a zigzag course.

In these vessels corrosion takes place if the gases are not sufficiently dried, acid mist is deposited in the tubes and eventually makes a hole,  $\text{SO}_2$  gases then pass through to the  $\text{SO}_3$  gases and go through the rest of the plant unconverted and unabsorbed, becoming a dead loss. If this action takes place it can be detected as follows :—

- (1) By a high acidity of the exit gases as tested by absorption in iodine or caustic soda.
- (2) By the production of a white mist leaving the exits of the absorption towers.
- (3) By a strong smell of  $\text{SO}_2$  in the acid or oleum produced.

By the action of this acid mist on the tubes, and other iron used in the plant, whatever arsenic is present in the iron is liberated as  $\text{AsH}_3$ , this is absorbed by the platinised mass as  $\text{As}_2\text{O}_3$  and causes permanent poisoning, which results in a decreased percentage conversion with a corresponding drop in efficiency.

Instances are known where the tubes have become so corroded that the iron sulphate formed has blocked some of them completely; it is this also which makes it a necessity to have all coke packed into filters 3, 4 and 5 properly dried, because efficient drying of the gases in the drying towers is useless if they are afterwards passed over wet coke; this also, applies to the coke in the grease catcher.

Wet coke in these vessels is known to be responsible for the formation of holes in the heat exchanger tubes of at least three units.

(11) **Heater-cooler (inner tubes).**—The purified  $\text{SO}_2$  gas mixture, coming at atmospheric temperature from the grease catcher, and having had its temperature raised to approximately  $180^\circ \text{C}$ . during passage through the heat-exchanger, received additional heat while passing through the inner tubes of the heater cooler. Gases leave these inner tubes or U pipes at approximately  $380^\circ \text{C}$ . and pass back to the converter house by a 15 inch steel pipe, which is connected to two 10 inch branches inside the converter house by means of 15 inch by 10 inch T piece. That is, the two 10 inch mains branch off this 15 inch main and proceed in opposite directions, half the gases passing each way. At each extremity of these 10 inch pipes a 10 inch by 10 inch T piece is fitted, the branch outlet of each connecting to the preheater inlet header. The end flange when normally running is blanked off, but when drying out the mass in the converter when starting operations, this flange is coupled to a 15 inch portable Sirocco fan. The second flange of this 10 inch by 10 inch T piece is connected to the inlet pipe of the converter, so that the preheater can be put out if temperatures are sufficiently high for optimum conversion. After leaving the heater cooler the gases divide again into two 10 inch mains and carry on through the rest of the plant in two equal portions. They pass either to the preheater or to the converter.

(12) **Preheaters.**—There are two preheaters to each unit, and they are similar to the heater cooler already described except that the tubes

# GRILLO OLEUM PLANT.

## REHEATER AND CONVERTER HOUSE.

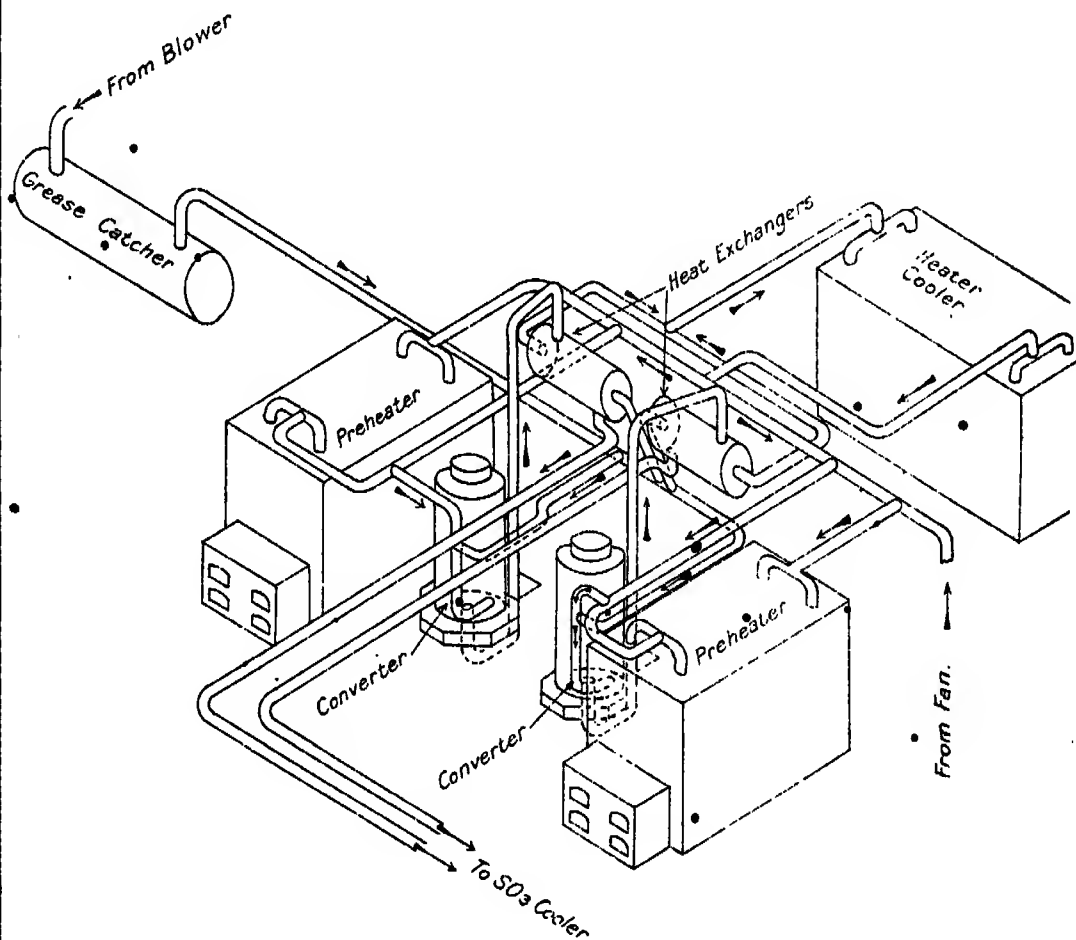


FIG. 20.





H.M. FACTORY QUEEN'S FERRY.  
 SHEWING SECTION OF CONVERTED AT  
 GRILLO OLEUM PLANT.

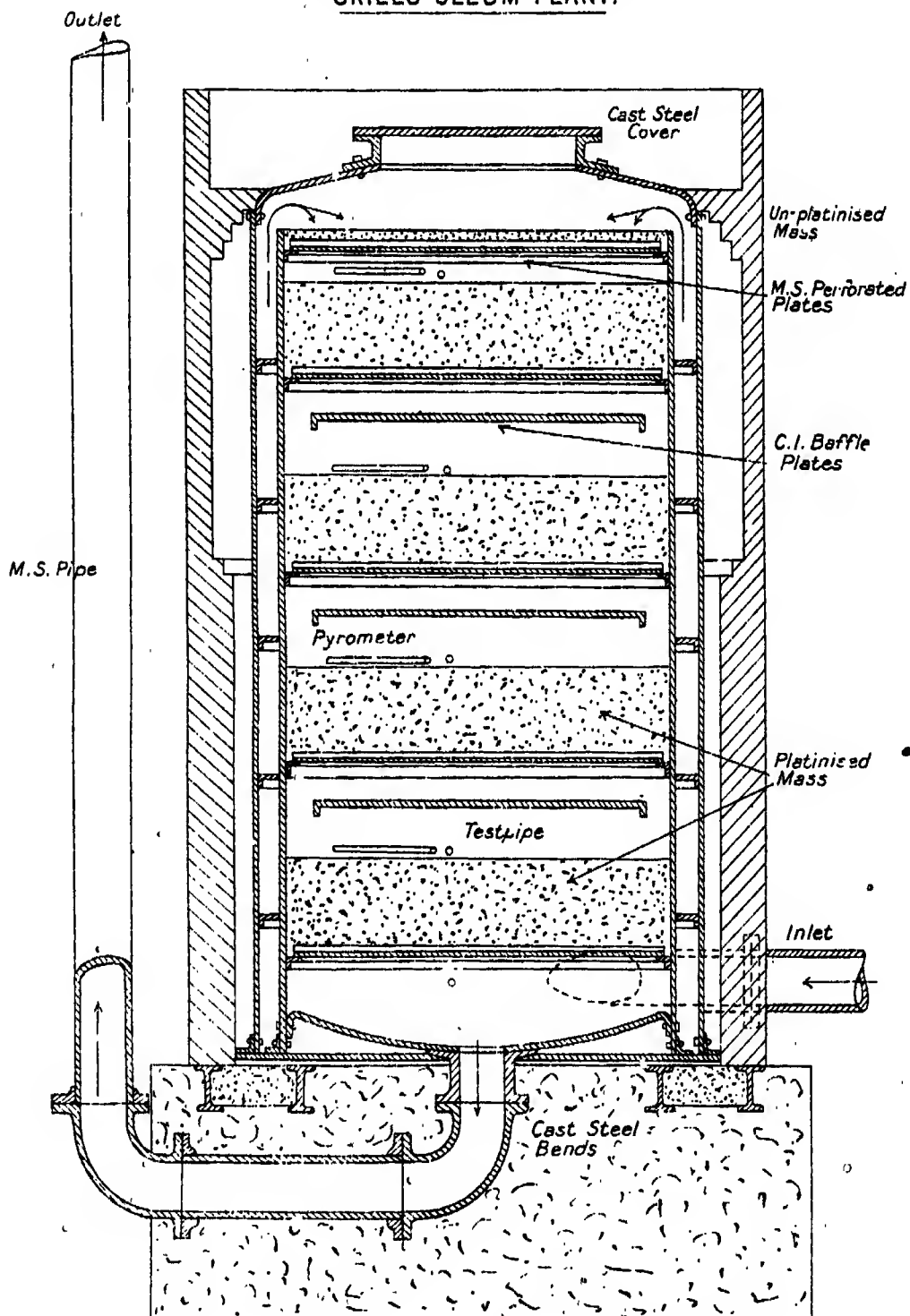


FIG. 21.

Scale 0.395 in. = 1 ft.

are heated by coal fires instead of the gases from the sulphur burners. The total heating surface of the pipes is approximately 1,100 square feet.

The preheater is only used when starting up the plant or when running on low sulphur charges in the burners. With high charges of sulphur sufficient heat is generated to heat the  $\text{SO}_2$  gas passing through the tubes to such a temperature that the preheater is unnecessary.

With the same percentage of  $\text{SO}_2$  in the gas leaving the burners (usually about 11 per cent.) the temperature of the burner gas is a constant, regardless of the quantity of sulphur burnt, but with larger sulphur charges the temperature of the gas passing through the system is better maintained for the reason that the radiation losses are distributed over a larger volume of gas. With large sulphur charges the gas passes direct to the converter without going through the preheater.

Occasionally the temperature is too high for optimum conversion and it is then necessary to reduce the temperature. This is attained by introducing cold gas from the 15 inch main from the grease catcher into the 10 inch main just before entering the converter.

(13) **Converter (Figs. 20 and 21).**—There are two converters for each unit, each converter consisting of one shell inside another. The inner shell is of mild steel, 6 feet 6 inches diameter inside by 12 feet 8 inches high, made from  $\frac{3}{8}$  inch plates. The outer steel shell is 7 feet 4 inches in internal diameter insulated from the atmosphere with slag wool, and an outer casing of  $4\frac{1}{2}$  inch brickwork. The lower extremity is closed by means of a  $\frac{1}{4}$  inch plate, which is provided with a cast steel seating for the 10 inch diameter outlet pipe situated in the centre of the plate. The flange of the pressed plate comes in contact with the inner surface of the shell. The upper end of the inner shell is left open to receive the incoming gases. The converter is arranged to accommodate four independent layers of the platinum contact mass. These mass layers rest on  $\frac{3}{16}$  inch perforated plates, are 14 inches to 16 inches thick, and each weighs approximately 2,500 lb. The converter has five perforated plates, the upper one being placed 3 inches below the gas inlet and serves to distribute the incoming gas. In some cases a thin layer of unplatinised mass (about 200 lb.) has been placed on the topmost perforated plate which then acts as a filter. Beneath the perforated plates carrying the first, second and third layers is placed a cast-iron baffle plate 5 feet 8 inches diameter and  $\frac{1}{2}$  inch thick, the space between the perforated plate and baffle plate being  $8\frac{1}{2}$  inches. These baffle plates rest on angle-iron, and being only 5 feet 8 inches diameter, allow an annular space of 5 inches wide round the plates through which the gases must pass before going through the next layer of mass.

• In passing through the converter the gases are raised considerably in temperature, due to the heat of reaction accompanying the conversion of  $\text{SO}_2$  to  $\text{SO}_3$ . By means of the baffle plates under the layers this heat of reaction is conveyed to the sides of the shell, and so heats up the gases passing between the two shells previous to entering the converter at the top.



The hot gases enter the outer shell by means of a 10 inch diameter pipe arranged at a tangent. Gases passing around the annular space of false wall between the two steel shells take an irregular spiral course between 3/16 inch baffle plates. The gases thus pass upwards, then down through each of the four layers, finally passing out as an  $\text{SO}_3$  gas mixture through the 10 inch diameter pipe connected to the bottom of the converter.

To prevent radiation losses, a brick casing is provided to the converter and the space between the outer shell and this casing is filled in with slag wool or other suitable insulating material.

The  $\text{SO}_3$  and air leave by the 10 inch diameter pipe around the inner tubes of the heat exchanger previously described. From the heat exchanger the gases are led out of the converter house by a 10 inch pipe to the  $\text{SO}_3$  cooler.

The gases enter the converter at about  $320^\circ \text{C}$ . and arrive at the top at  $360^\circ\text{--}370^\circ$ .

If the gases reach the first platinised layer at about  $360^\circ$  and do not contain more than 5 per cent. of  $\text{SO}_2$ , 97 per cent. conversion can be obtained without any further control of temperature.

*Conversion.*—The conditions necessary for good conversion, *i.e.*, 96 per cent., are :—

(1) Uniform burning of sulphur at the burners in order to yield a steady 5.0 per cent.  $\pm$  0.2 per cent. at the converters.

(2) Pure gas.

(3) Low temperatures in the converters, *i.e.*, no temperature to exceed  $480^\circ \text{C}$ .

(4) Exit temperature of gases from converters not higher than  $410^\circ \text{C}$ .

(5) Steady temperatures.

(1) and (2) These have already been dealt with in detail.

(3) The temperature at which conversion begins is a function of the velocity of the gas.

The higher the velocity the higher the temperature required to start conversion.

On a 35 lb. charge the velocity is 4.0 feet per second through the converters and conversion starts at  $360^\circ\text{--}370^\circ \text{C}$ .

On a 70 lb. charge the velocity is 8.0 feet per second and conversion starts at  $360^\circ\text{--}380^\circ \text{C}$ .

On an 80 lb. charge the velocity is 9.2 feet per second and conversion starts at  $380^\circ\text{--}400^\circ \text{C}$ .

The only means of obtaining low temperatures throughout the converters on a 70 lb. or higher charge is to keep the gases as they reach the first platinised mass at as low a temperature as possible, while still obtaining the necessary conversion on the first layer, this temperature is  $360\text{--}370^\circ \text{C}$ .

Several conditions come into play here, the speed of the gas is so high and the temperature is so low that the first layer is not able to

attain its maximum converting power, as denoted by the relatively small rise in temperature of the gases as they leave this layer; by thus throwing the conversion on to the lower layers the heat evolved during the reaction is distributed more evenly over the various layers and prevents any one of them reaching an excessively high temperature.

(4) By raising the temperature of the gases going on to the first layer to say  $390^{\circ}$ – $400^{\circ}$  C., a much greater conversion takes place on that layer—the second and third become excessively hot and outside the 98 per cent. conversion zone of  $370^{\circ}$ – $470^{\circ}$  C. The exit temperature also gets beyond the 100 per cent. conversion temperature of  $410^{\circ}$  C.

(5) The maintenance of steady temperature conditions in the converters, as opposed to oscillating temperatures, means the difference between good and moderate conversion, or, say, the difference between 96 per cent. and 95 per cent. The gases reaching the first layer can easily be kept within the limits  $360^{\circ}$ – $370^{\circ}$  C., and that is the only regulation required, all other temperatures adjust themselves automatically.

*Temporary poisoning of the contact mass.*—This temporary poisoning is caused by halogen in the gas and can be more easily remedied than the more serious arsenic poisoning, which necessitates the removal and special treatment of the contact mass.

Temporary poisons such as chlorine and chlorine compounds have the same effect on conversion as an increase in velocity of the gases, but in a more marked degree, that is to say, a higher temperature is needed to start conversion; in some instances it has been necessary to raise the temperature to  $420^{\circ}$  C. in order to get the right percentage conversion on the first layer. This poisoning may extend to all the layers, and in some cases the effect is so marked that the temperature becomes too low and conversion practically ceases.

The evil effect will be first apparent in the drop in temperature recorded by the pyrometer under the top layer indicating less heat of reaction.

It is not strictly correct to say that temporary poisoning stops conversion, because so far as has been proved, it is only a matter of temperature, and if the temperature of the gases can be brought up quickly by means of the preheater the percentage conversion can be prevented from falling excessively. As a rule, however, it is not possible to reach this high temperature of  $420^{\circ}$  C. in time to save the situation.

The poison is removed by roasting, *i.e.*, by blowing a large quantity of air at  $450^{\circ}$  C. through the converters for about four hours with the plant stopped. When the roasting has taken place it is found that the temperature at which conversion can start gradually approximates to its former figure.

Naturally, means must also be taken at once to prevent a recurrence of the trouble by more efficient purification. This can be effected by using weaker acid (50 per cent.  $\text{H}_2\text{SO}_4$ ) in No. 1 scrubber, or, if this be not efficient, by spraying water down a header of the  $\text{SO}_2$  cooler.

At one period much trouble was caused due to an excessive amount of chlorine in some lots of sulphur. A Gaillard spray was very efficient in washing out the chlorine, but of course there was a loss of sulphur dioxide too, which lowered the overall efficiency of the plant.

(14) **SO<sub>3</sub> coolers.**—The gases from the converter pass into the heat exchanger, surrounding the tubes containing the SO<sub>2</sub> gases on their way to the heater cooler, and then pass to the SO<sub>3</sub> coolers.

These are composed of two batteries in parallel; each battery consists of a first header which delivers into eight 6 inch horizontal U tubes, each 30 feet long, and a second header which collects the gases again from the other end of the tubes, these are made of mild steel. The second header delivers the gases by means of a 10 inch main to the absorption towers.

The temperature at which the gases enter the SO<sub>3</sub> coolers is not important, but they must leave above 30° C., or SO<sub>3</sub> will be deposited as a wax-like solid in the tubes and obstruct the passage of the gases. Solid SO<sub>3</sub> here is very difficult to dislodge.

The method of cooling the gases is important, ordinary air cooling is the best, as no ill-effects arise from it. Water cooling has disadvantages. When cold water reaches the steel tubes, it causes local cooling of the SO<sub>3</sub>, some of this polymerises and, as it is much less soluble in the absorbing acid and oleum than the simpler molecule, passes through the absorption system and escapes as a white mist.

So far as absorption itself is concerned, 100° C. is an excellent temperature for the gases leaving the SO<sub>3</sub> coolers and entering the absorption system; the high temperature does not produce any escape owing to vapour pressure, &c. It is, however, inadvisable because of the corrosive action of the hot acids on the containing vessels.

With high charges in summer-time it is difficult to keep the temperature of the SO<sub>3</sub> down to, say, 60° C. without causing polymerisation, and a more extensive system of air-cooling would be an advantage.

On the other hand, with low charges in winter, the SO<sub>3</sub> reaches the absorption towers at too low a temperature, *i.e.*, in the neighbourhood of its freezing point, and under these conditions only one-half the cooling plant is required.

When water is used as the cooling medium, it should be applied to the tubes as a very fine spray.

(15) **Absorption towers (Figs. 22, 23 and 24).**—There are six towers per unit, two series of three, and each series deals with the gas from one converter. The towers which are built of mild steel are 24 feet in height and 6 feet in diameter; they are lined with acid-proof tiles and filled with clean-graded quartz resting on a grid supported on cast-iron pillars. A cast-iron distributing plate sits on the quartz and the cover of the tower has a combined feed and sight box for the circulating acid.

A circulating tank which acts as a reservoir for acid is fixed a few feet away from the base of each pair of towers. These tanks are lined with acid-proof brick, and measure internally roughly 7 feet by 5 feet by 4 feet. The absorption tower is provided with two openings at the





bottom, one to accommodate the gas entering by the 10 inch pipe and the other to drain away acid which has passed down the tower. These acid run-offs are of 6 inch cast-iron square flanged piping.

The gas passes up the first tower, out at the top, down by a 10 inch pipe into the second tower, up this tower, then up the third tower, finally issuing to the atmosphere by a 10 inch pipe passing through the roof of the house.

A 6 inch cast-iron cooler built up of 9 foot lengths and bends and 550 feet long in all is used for cooling the acid used for absorption.

A 5 inch steel cooler, similar to the above, is used to cool the circulating oleum. Acid of 98 per cent. strength is circulated over the second and third towers in each series and absorbs the  $\text{SO}_3$  which passes tower 1, this acid runs into one common 6 inch cast-iron pipe at about 100 per cent.  $\text{H}_2\text{SO}_4$  and is reduced to 98 per cent. again by the addition of weak  $\text{H}_2\text{SO}_4$  or water through a sight box, it then runs through the acid cooler back to the circulating tank, whence it is pumped to the top of the towers again and the process repeated.

Part of this acid is allowed to gravitate from the first circulating tank to the second, and from the second into the third,\* at the base of the oleum tower in this tank it meets 26 per cent. oleum which is running in from the oleum tower, the two mix with the 22 per cent. oleum already in the tank to make more 22 per cent. oleum. Part of this runs in a constant stream to storage and represents the make, this run off is also the cause of the gravitation from the first two tanks. Oleum is pumped from its circulation tank over the first tower, or oleum tower, in each series, absorbs  $\text{SO}_3$  while trickling down, arrives at the base at about 26 per cent. oleum, runs through the oleum cooler and back into the oleum tank, where it meets the 98 per cent. acid as previously described, and the whole process is repeated. About 4 tons per hour is pumped over each tower, the minimum should not be less than 3 tons or the absorbing acid and oleum will get too strong and less efficient for the purpose.

Centrifugal pumps are used when the oleum pumped over the first two towers is 20-22 per cent. approximately; 90 per cent. of the  $\text{SO}_3$  in the gases can be absorbed provided enough oleum is circulated. The tonnage required varies with the sulphur charge, but should be enough to keep the oleum running off from the towers not higher than 26 per cent. In order to obtain good absorption all that is required is:—

(1) To maintain the oleum in circulation between 20 per cent. and 22 per cent.

(2) To maintain the acid between 98 per cent. and 99 per cent.

(3) To pump enough of the above over the towers.

Diagrams of the absorption system are given in Figs. 24A and 24B.

Acid and oleum coolers (Figs. 22, and 24).—The acid and oleum coolers were described in the preceding section.

\* See pages 84 and 114.

The oleum coolers leave nothing to be desired, they are ample in proportion and not the slightest trouble has been entailed by them. The cost of maintenance is nil.

The 98 per cent. acid coolers are sufficiently large to meet all needs and give all the cooling surface required.

The following points, however, on these have been made :—

(1) Every three months the coolers on units using as feed concentrated spent acid from TNT nitration processes silt up and require washing out. This practice has an injurious effect on the joints of the coolers.

(2) There is considerable trouble with joints leaking on the coolers. In order to carry out repairs to (2) it is necessary to stop the plant and pump the cooler empty. This operation takes several hours, and when the unit is running regeneratively there is danger of the plant getting too cold.

Two measures could be adopted to overcome this :—

(1) The use of the cooler pipes with round eight-hole flanges, similar to those used on the oleum coolers, instead of the square four-hole flanges.

(2) Instead of only one cooler being used for cooling the 98 per cent. acid from the four end towers, two coolers could be installed, one for each pair, and when repairs were necessary on any cooler that cooler and its towers could be cut out and the plant could carry on until the repairs were executed.

With regard to the silting up of the towers, which also happens, the latter need to be washed out every few months, this is done by completely disconnecting them from the gas inlet pipes and coolers and washing, with fire hoses from the top.

When a unit starts up again, after washing the towers, a heavy mist is noticed leaving the absorption tower exits. This gradually dies away and becomes invisible in about 72 hours. It is the usual mist which is always formed when moisture and gaseous  $\text{SO}_3$  come into contact. Attempts have been made to absorb it by means of acid and oleum of various strengths, but without success.

In the ordinary course of events, when the absorption tower exits fume, a quick and convenient test of the cause is the colour of the fume.

**Efficiency.**—Unless strict attention is paid to details the efficiency of a Grillo plant decreases very quickly. It needs only a little slackness to cause a drop from 95 per cent. to 90 per cent.

(1) Acid leaks should be stopped immediately, and their promotion discouraged.

(2) Strict attention should be given to regularity in sulphur burning, gas purification, and control of converters in order to obtain the maximum conversion.

(3) Loss of  $\text{SO}_2$  in the scrubbing system, by solution of the gas in the circulating acid, should be minimised by covering the tanks and drawing the secondary air for the plant over them.

# GRILLO OLEUM PLANT.

## ABSORPTION HOUSE.

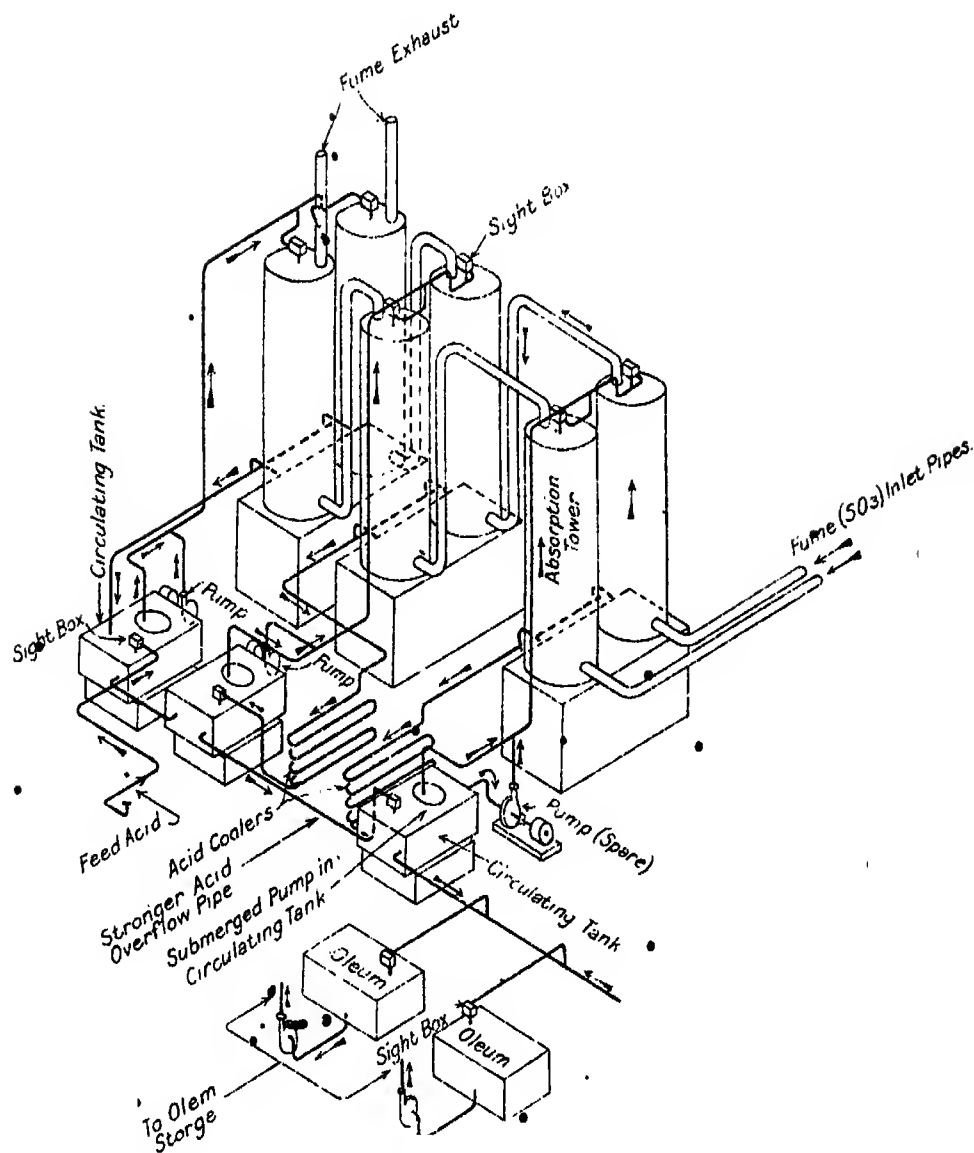


FIG. 24.





# H.M. FACTORY QUEEN'S FERRY. — GRILLO-CIRCULATION SYSTEM FOR OLEUM.

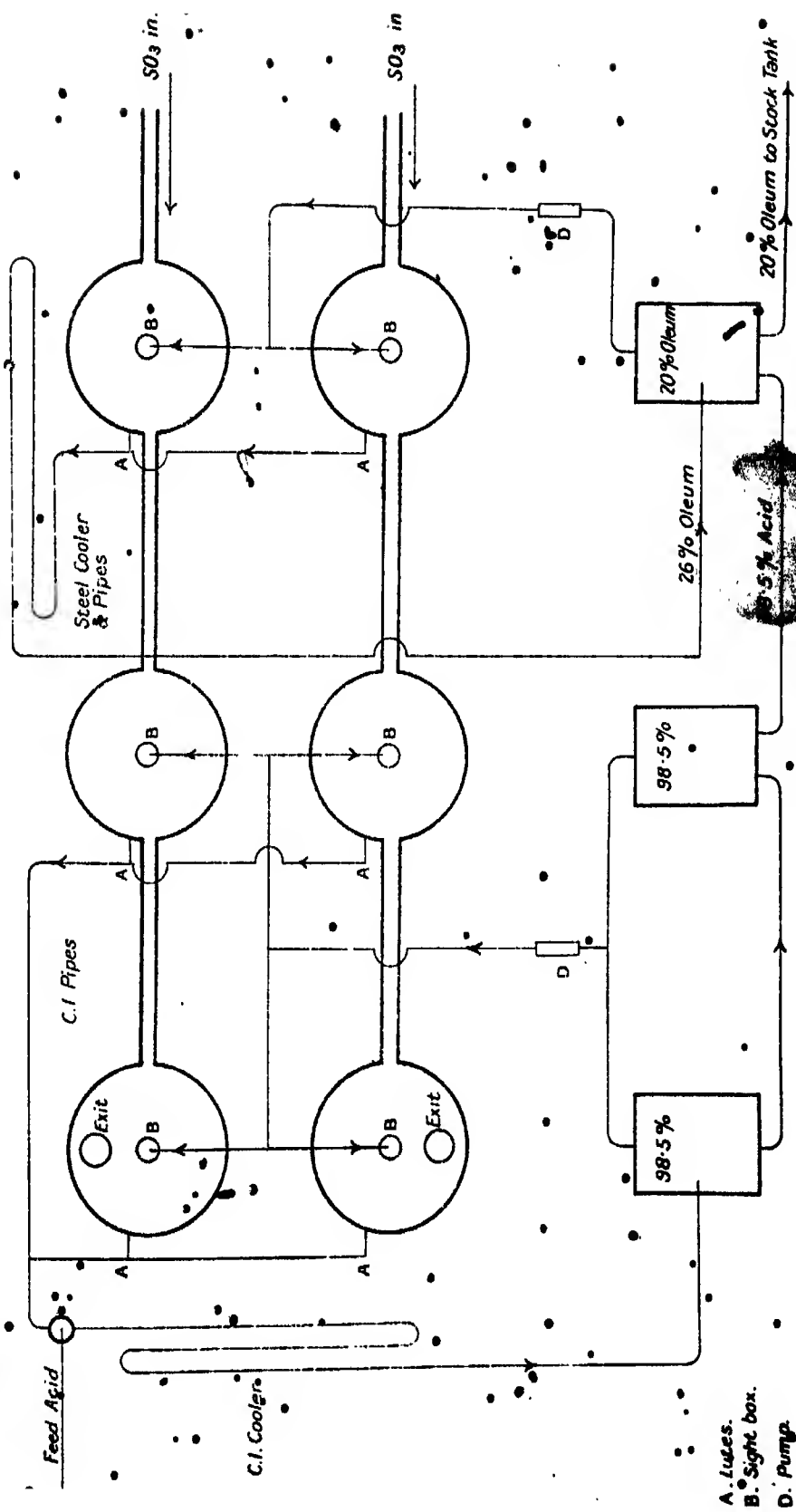


FIG. 24A



# H.M. FACTORY QUEEN'S FERRY — GRILLO CIRCULATION SYSTEM FOR 98.5% ACID.

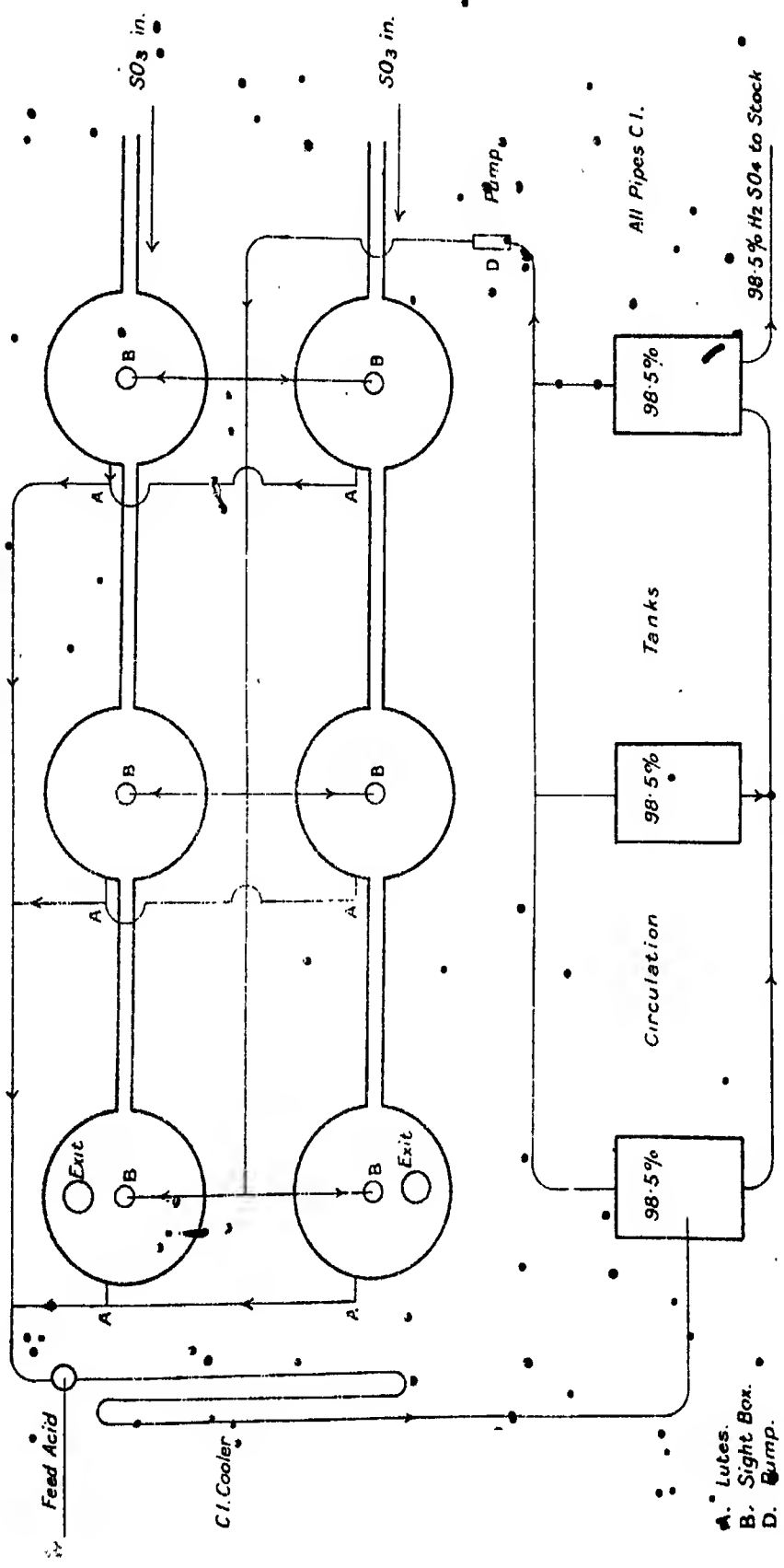


FIG. 24<sup>B</sup>



(4) Care should be taken to keep the absorbers working as perfectly as possible, particularly in the night time.

(5) All gas and water exits and effluents should be tested by the continuous method.

The following is a list of efficiency and losses as calculated from chemical control tests:—

	Per cent.
Efficiency	95.8
Unconverted $\text{SO}_2$	3.5
Loss at scrubbing towers	0.4
Loss in effluent water	0.2
Loss in absorption system	0.1
Loss in sulphur ash	—
	<hr/> 100.0 <hr/>

The efficiency during the same period as calculated from the sulphur burned, feed acid consumed and oleum produced was 95.3 per cent., showing a difference of 0.5 per cent. This was most probably due to errors in measurement, but the closeness of the figures shows the advantage to be gained by a careful control of losses from all sources.

**Power consumption of pumps.**—The total power consumed by pumps, on one unit for all purposes, is 12 k.w.

#### PRODUCTION OF MAGNESIUM SULPHATE MASS

The method adopted for the production of this mass, which serves as the carrier of the finely divided platinum, the catalytic agent, comprises:—

(1) Calcination of the crystallised magnesium sulphate  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , in shallow cast-iron pans.

(2) Crushing and grinding of the whole of this first cake.

(3) Production of second cake by mixing the dust with water in another similar pan and calcining.

(4) Crushing and sizing of the second cake.

##### 1st Calcination.

The time required to convert the crystalline salt into a dry cake is about seven hours.

The cake is detached from the bottom of the pan by long chisel-pointed steel bars. When cooled it is crushed and reduced in a disintegrator to a fine powder which contains from 12–14 per cent. of moisture.

##### 2nd Calcination.

In the production of second cake, two kinds of material are used—dust from 1st calcination and dust made by grinding the fines from the crushing of the second cake previously made. First cake dust gives excellent second cake, but dust made from second cake cannot be used alone to make satisfactory second cake again. The two kinds of dust

are accordingly put into an open bin divided into two by a partition, each kind being put separately into its own part of the bin.

When the pan is charged, two buckets of the first dust and two of the second are put on to a hot pan and water is added from a watering-can with a long spout, but without a rose. The dust is thoroughly mixed in with the water by means of a long-handled steel garden rake 15 inches broad. About 150 lb. of dust and  $2\frac{1}{2}$  buckets (75 lb.) of water are added altogether in order to obtain a mixture of the consistency of thick cream. The water evaporates rapidly during and after the mixing, and the raking is continued to assist the formation of the hard cake at the bottom and to break up any crust that may form at the top, until it is baked red-hot nearly all over. It is then broken up with iron rods, left to cool and crushed.

The average time required for a charge is about five hours, and the weight of cake obtained is nearly equal to that of dust put in the pan.

Before crushing care must be taken that the crusher is set to give, in this case, the coarsest possible product. The crushed material is transferred by hand to the hopper of the trommel, from which three sizes are obtained: (1) finished mass,  $\frac{1}{2}$  inch to  $\frac{1}{4}$  inch; (2) fines,  $\frac{1}{4}$  inch and less; and (3) oversize above  $\frac{1}{2}$  inch. The feed to the trommel must be continuous and not intermittent, to prevent fine material passing over the finer of the two screens and passing out with the finished mass. Oversize amounting to about 6 per cent. of the total weight crushed is returned to the crusher. The fines are ground in the disintegrator as fast as they come from the screen. The finished mass obtained is weighed as it is taken to the bins and the dust from the disintegrator is weighed also.

The percentage of moisture is rarely found to be below 9 or above 10.

Unplatinised mass weighs about 46 lb. to the cubic foot.

**Platinisation.**—Before platinisation all mass is riddled carefully over  $\frac{1}{4}$  inch riddle, to remove fine stuff which may have passed the finer screen of the trommel or may have been produced in transport or storage. The riddled material is then weighed out into iron cans, 100 lb. in each. Two of these cans are emptied into each platinising stone-ware bath or tray and the mass is spread out in an even layer by means of a wooden rake.

In 200 lb. of mass there are very nearly 180 lb. of anhydrous sulphate. The amount of platinum chloride required to give the desired percentage of platinum, reckoning on the 180 lb. of anhydrous sulphate, is weighed out on a pair of scales, having one pan of enamelled iron or earthenware. Acid-proof enamel should be used as the ordinary enamel is rapidly eaten away.

The weight of water required to secure even distribution varies between 20 and 30 lb., but is generally about 22.5 lb. (2 gallons and 1 quart). Considerable heat is evolved during platinisation, and care should be taken that mass should not be used which has come directly from the mill and still retains heat. It has been found that more regular

results are obtained where two bins are available by putting all freshly-made mass into one bin and drawing for platinisation from the other.

The spray by which the solution is applied consists of four fine glass jets connected by short lengths of rubber tube to a glass tube having four short branches and one longer one sealed on in the form of a fork. This arrangement is enclosed in a wooden case from the end of which the jets project. The longer branch of the fork is connected by means of a long black rubber tube and a glass syphon to the bucket containing the solution. This bucket can be raised above the bath by pulleys and a sash cord, and the rate of flow of the solution can accordingly be varied at will.

About half of the two gallons or so of solution is poured into the bucket and hoisted to about 4 feet above the level of the bath. Spraying is begun and as soon as the surface of the mass has been covered the surface layer is raked to one end and spraying is continued. This goes on until all the mass has been raked into a pile at one end of the bath. The pile is then turned over to expose the mass at the bottom, which so far has not been covered. By this time the first half of the solution has probably run out. The second half is then put in and spraying is continued, the rake being driven evenly through the mass from one side to another in a regular manner until all this solution has also been used. At the finish the mass should appear wet. It should be turned over with the rake for about five minutes after spraying has finished and allowed to remain on the trays for at least eight hours before removal to the converters.

**Filling the converters.**—The percentage of platinum used at Queen's Ferry is 0.3 for the upper three layers of the converter and 0.35 for the top layer. These percentages are on anhydrous magnesium sulphate. In one case the richer layer was placed at the bottom, but no difference in conversion between the two converters of this set has so far been noticed.

Before filling, the inside of the converter is thoroughly cleaned out with wire brushes, and a current of air is blown through to remove all dust. The bottom perforated plate is then put in and about 200 lb. of coarse unplatinised material (oversize from the crusher) is spread out on it. This forms a layer about 2 inches deep and lessens the risk of platinised mass falling through the holes in the plate.

As the mass is platinised it is stored on the spare trays in the platinising room in lots of 2,200 or 2,400 lb., and is removed from them as required in enamelled iron buckets. These are hoisted into the converter by means of a rope and pulley. Great care is taken to secure an evenly distributed and level layer. A small iron rake is useful for this; the final levelling can be done with the flat of the handle.

The bottom layer being complete, the baffle plate and its trestle are put in. Filling of the second and third layers proceeds in the same way, except that no oversize is used. Before filling the top layer, however, the trestle which is to carry the uppermost perforated plate must be put in, as it cannot be afterwards inserted through the manhole



without removing one of the quadrants of the plate on which the top layer is to rest.

The weights of mass filled in have been in general as follows :—

Bottom layer	{ 200 lb. oversize on bottom plate.
	{ 2,350 lb. 0.30 per cent.
Second layer	2,550 lb. } 0.30 per cent. anhydrous mass plati-
Third layer	2,550 lb. } nised=9,000 lb.
Top layer	2,550 lb. 0.35 per cent.

On the uppermost perforated plate about 180 lb. of ordinary unplatinised mass are placed, to act as a coarse filter to the incoming gas.

With this filling, the depth of layer is in each case about  $17\frac{1}{2}$  inches; from the top of the layer to the upper surface of the baffle plate above it, should be about  $8\frac{1}{2}$  or 9 inches.

When in the converters the contact mass is dried by means of hot air. It is then ready for use as a catalyst.

The qualities desired in the finished mass are :—

- (1) Tensile strength as high as possible.
- (2) Pieces of uniform size.
- (3) Uniform distribution of the platinum.
- (4) Platinum deposited as completely as possible on the surface of, and not inside, the pieces.
- (5) Not too porous.

**Recovery and purification of magnesium sulphate and platinum from old contact mass.**—The dissolving tank (capacity, 1,400 litres) is three-quarters filled with ordinary water, and a sieve made from a carboy cradle lined with wire gauze (28 mesh to 1 inch) is lowered into the tank by means of a pulley until half submerged in the water. This sieve retains the larger particles of iron scale, &c., while allowing the platinum to pass through. The contact mass is then placed in the sieve by bucketsful, and as the  $\text{MgSO}_4$  passes into solution more is added until 120 kilos (approx.) are dissolved. The sieve is then hoisted out of the solution, which is then allowed to stand for at least three days. At the end of that time the insoluble matter has fallen to the bottom of the tank, beneath the level of the tap from which the clear liquid is drawn off into a lower tank, where a further settling of three days is allowed. From this tank it is run through the tap into a lead-lined box, in which it remains for two days.

**Purification of the magnesium sulphate.**—The solution is then syphoned, without disturbing the lower stratum of the fluid, into a wood-lined box, which is fitted with steam and air pipes. After being heated by steam to a temperature of  $60^\circ \text{C}$ ., magnesium oxide (10 kilos approx.) is placed in a suspended sieve (five meshes to 1 inch) as in the case of the first dissolving tank, and the whole agitated with air until a sample of the filtered fluid gives an alkaline reaction and shows no precipitation or colouring with  $\text{H}_2\text{S}$ . Steam and air are then shut off and the liquid allowed to settle. After 24 hours the  $\text{MgSO}_4$  solution is

usually clear, when it is decanted into an egg and blown to a feed box in the concentrating plant. The lead lining of this box is painted with black enamel. From the box the solution is run into a series of coal-heated galvanised concentrating pans, five in number, and when a film appears on the surface of the front and hottest pan the contents of that pan are syphoned into a crystallising pan, where on cooling  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  crystallises out. The crystals are drained and heated on a cast-iron pan where water is driven off until a hard mass containing 13 to 16 per cent.  $\text{H}_2\text{O}$  is formed. This is removed and broken in a crushing machine into pieces of the requisite size. Dust and particles too small for grading are made into a paste with  $\text{MgSO}_4$  solution, and dried on the cast-iron pan in the same manner as the crystals.

**Purification of platinum.**—When the clear fluid is drawn off from the dissolving tank, it is again filled up with water, and the process of solution continues (120 kilos. (approx.) of contact substance being dissolved at each operation) until a complete shelf has been broken up. The insoluble matter remaining at the bottom of the tank is washed two or three times with water to remove  $\text{MgSO}_4$ , and finally run through the lower faucet, which is fitted with a rubber pipe closed by a brass clip, into an earthenware crock (200 litres capacity). This crock is placed in a steam-heated water bath and its contents treated for 48 hours with strong commercial hydrochloric acid at as high a temperature as possible, at the same time being agitated with air.

It is then allowed to cool and settle, when the hydrochloric acid solution is syphoned off into a larger crock (400 litres) in which scrap iron is constantly kept. The crude platinum mass is washed repeatedly with water until the washings are comparatively free from soluble Fe. (Owing to the slight solubility of platinum black in hydrochloric acid under certain circumstances, and to the possibility of free chlorine in commercial acid, in all cases where platinum—whether impure or otherwise—is treated with hydrochloric acid, the washings are subjected to the action of scrap iron, whereby any platinum, which may be in solution is reduced by hydrogen, thrown down and collected.)

The crude platinum mass is then treated with hot aqua regia, at the same time being agitated by air until the residue which remains undissolved shows no platinum. On settling and cooling the clear solution is syphoned into porcelain basins, while the residue is washed in filter until free from  $\text{PtCl}_4$ . The clear solution and washings are concentrated to a small bulk on a steam bath, 30 c.c. of 90 per cent. sulphuric acid being added to remove lead. The concentrated fluid is then transferred to a sand bath, where it is dried—additions of hydrochloric acid being made until the resulting dry mass is free from nitric acid. This mass is then dissolved in water, filtered, hydrochloric acid added to the clear solution, from which the platinum is then removed by the action of scrap iron (wrought iron rails). The platinum black is collected and boiled with strong hydrochloric acid on a sand bath until only traces (less than 3 per cent.) of iron remain undissolved.

In practice it is found impossible by the action of boiling concentrated hydrochloric acid to remove iron entirely from platinum black in this

form. Hence the necessity for the subsequent precipitation by ammonium chloride by means of which it is possible to remove the residual iron completely.

It is then washed with water until free from chlorine, dissolved in pure aqua regia, again dried and freed from nitric acid, dissolved in water, acidified with hydrochloric acid, and precipitated with ammonium chloride. The  $(\text{NH}_4)_2\text{PtCl}_6$  is allowed to settle and, after the supernatant fluid has been syphoned off, is transferred to a Buchner funnel, where it is washed with 5 per cent. hydrochloric acid solution until the filtrate is free from iron. The precipitate is then dried on the sand bath, and ignited in a fireclay crucible in an atmosphere of sulphur dioxide. The resulting pure spongy platinum is weighed and dissolved in aqua regia, and its solution, freed from nitric acid, is ready for the preparation of contact substance.

The iron scales, &c., which are retained by the sieve on solution of the magnesium sulphate in the first dissolving tank may still contain a little platinum, most of which can be removed by washing it in small quantities in a basin with a constant stream of water. The whole is agitated, and the lighter and smaller particles, representing the platinum, are allowed to pass with the overflow water into one of the settling tanks from which it may be collected on settling. The heavy portion remaining in the basin is rejected.

From time to time, say, after two or three shelves have been treated, any matter which may have collected in the bottom of the lower settling tanks is washed out and the sediment placed in the top dissolving tank.

The hydrochloric acid washings of the  $(\text{NH}_4)_2\text{PtCl}_6$  precipitate obtained in the second stage of platinum purification are treated with scrap iron, and the platinum black precipitated is added to the platinum belonging to the next shelf before purification.

**Separation of iridium and platinum.**—Where a shelf has originally been impregnated with solution of platinum and iridium scrap, the presence of iridium is first seen from the difference in colour of the precipitate on adding ammonium chloride to the platinum solution. Ammonio-platinic chloride,  $(\text{NH}_4)_2\text{PtCl}_6$ , unmixed with iridium, is of a lemon yellow colour, while, if iridium is present, the colour is a light reddish brown. As ammonio-platinic chloride is less soluble in hydrochloric acid than the corresponding iridium salt, the latter may be partially removed by repeated washings with hydrochloric acid, 5 per cent., when the ammonio-platinic chloride approaches more to its normal colour. On concentrating a sample of these washings a cherry red substance is deposited, showing a large proportion of  $(\text{NH}_4)_2\text{IrCl}_6$ .

The whole of the hydrochloric acid washings are treated with scrap iron, and the iridium is thrown down as a black precipitate which also contains platinum. To remove the last trace of iridium from the ammonio-platinic chloride after washing as above with dilute hydrochloric acid, it is necessary to dissolve the whole in as small a quantity of hot water as possible. The solution is evaporated to a fifth of its bulk, and on cooling 88 per cent. of the original platinum crystallises

out as  $(\text{NH}_4)_2\text{PtCl}_6$ , while the iridium salt, being more soluble in water, remains in solution, and may be removed as iridium black on adding scrap iron.

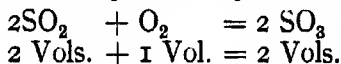
## CHEMICAL CONTROL

**Percentage conversion.**—The percentage conversion of  $\text{SO}_2$  to  $\text{SO}_3$  is estimated by determining the percentage of  $\text{SO}_2$  in the gases entering and leaving the converter. The Reiel method is used, viz., taking a known quantity of standard iodine solution and bubbling the gases through until all the iodine is reduced, using starch paste as an indicator; when corrections are made for temperature and pressure this method gives fairly accurate results.

A more accurate but longer method is employed as a check on the above. Vacuum bulbs of a known capacity are taken, filled with the gas under examination and the  $\text{SO}_2$  content absorbed in a known volume of standard iodine solution; the amount of iodine used is obtained by titrating back with sodium thiosulphate solution, and from this the  $\text{SO}_2$  present can be quickly calculated.

With the  $\text{SO}_2$  in the entrance and exit gases to the converter determined, the percentage conversion is then a matter of arithmetic.

It must, however, be remembered that a reduction in volume takes place in the converter according to the equation—



When this correction and corrections for temperature and pressure are made this method gives very accurate results.

**Moisture and acid mist.**—Moisture and acid mist in the gases are estimated by aspirating a known volume through tubes containing cotton wool and phosphorus pentoxide. Cotton wool filters the mist from the gases and  $\text{P}_2\text{O}_5$  absorbs the moisture.

**Chlorine.**—Chlorine in the gases is estimated by bubbling the latter through distilled water from a 1/6th orifice for a period of 24 hours continuously, boiling off the sulphur dioxide and precipitating the chlorine as silver chloride; the amount of chlorine present is too small to obtain any accurate quantitative figure.

**Arsenic.**—It has never been possible to find arsenic in the gases entering the converters, this is to be expected seeing that arsenic is not found in the sulphur used; nevertheless, a sample of the calcined sulphate mass, taken from a unit which had been running for 10 months, on analysis contained 50 parts of arsenic per million.

The sample was taken from the first tray of the converter, and it is presumed that acid mist had acted on the iron vessels and tubes, which generally contain arsenic, thus making  $\text{AsH}_3$ , which would burn to arsenious oxide and combine with  $\text{MgO}$  in the calcined mass.

**Waste gases.**—1. The gases leaving the absorption towers are aspirated through bottles containing a known quantity of standard

alkali together with a little hydrogen peroxide. From this the total acidity can be calculated.

2. The sulphur dioxide in the waste gases is estimated by the Reich method.

3. The difference between 1 and 2 gives the amount of sulphur trioxide in the waste gases.

4. The volume of gas is fairly accurately obtained by calculation, from the tons of sulphur burnt and the percentage of sulphur dioxide in the gases entering the converters. Correction being made for the elimination of 2.5 per cent. in the purification system.

#### SULPHUR DIOXIDE LOSSES IN PURIFICATION

Originally, at Queen's Ferry, these amounted to  $1\frac{1}{2}$  per cent. of the sulphur burned.

This quantity was reduced to 0.4 per cent. by covering the receiving tanks above and below the scrubbing towers with light wooden covers.

In this way the vapour pressure of the sulphur dioxide in the stagnant gas above the surface of the acid in the tanks was maintained at a comparatively high figure and losses were consequently reduced.

It has also been shown that as far as the middle and strong towers are concerned an acid flow of 10 tons per hour suffices.

The sulphur dioxide required to saturate this quantity of acid is obviously half that required to saturate a flow of 20 tons or more per hour.

Reduction of the quantity of acid will therefore bring about a corresponding reduction in sulphur dioxide losses.

By drying the secondary air before admitting it to the system a further reduction in the quantity of acid in contact with sulphur dioxide will be effected, and this in turn will still further cut down sulphur dioxide losses.

#### REPORT ON THE APPEARANCE OF A GRILLO UNIT AT H.M. FACTORY, QUEEN'S FERRY, AFTER FIFTEEN MONTHS CONTINUOUS WORK

Unit 3 was closed down and each section of the unit was opened up and examined, we summarise the results of the examination.

*Burners (chequer work).*—Slight deposition of iron oxide. The quantity of this was too small to cause any obstruction of the gas flow, and it was obvious that the burners could run for two or three years without any trouble from blockage of the chequer work.

Burners 1, 6 and 12 were opened up and examined and were all found to be quite clear from dust or blockage of any kind.

*Heater-cooler and flues.*—Very little deposit was found here—a scale approximately  $\frac{1}{8}$  inch in thickness had been formed on the heater-cooler pipes and this was removed.

*Pressure equaliser and blower.*—A small quantity of slime was found in this part of the system and this was washed out, first with water and then with a slightly alkaline solution.

The slime was probably formed during the period when acid mist was one of the chief troubles:

*Heat-exchanger.*—This was perfectly dry and free from slime.

*Converters.*—The top layer of unplatinised mass was perfectly dry, and on testing showed 30 parts arsenic per million. This was replaced by fresh unplatinised mass.

A small sample was taken from the first platinised layer and gave 10 parts arsenic per million.

At one period during the running of the unit, small quantities of arsenic were detected in the sulphur dioxide cooler drips, so that the sulphur has apparently contained traces of arsenic which, however, have never been detected in the control analysis which are always made on fresh consignments of sulphur.

The unit is once more in operation with a 95.8 per cent. conversion on a 70 lb. charge.

It is evident, therefore, that in spite of rough treatment during the earlier stages of operation of the Grillo, the plant is in perfectly sound condition after 15 months work.

#### • REPORT ON THERMAL VALUES AND EFFICIENCIES ON A GRILLO PLANT

##### Section I.—Burner balance.

"A Unit" run on 70 lb. charges. 12 burners.

*Heat generated per hour:—*

(1) From sulphur burned to  $\text{SO}_2$ —

$70 \times 12 \times .99 = 832$  lb. pure sulphur burned per hour

$\text{S} + \text{O}_2 = \text{SO}_2 + 71,080$  cal.

$\therefore 71,080$  cal. are liberated when 32 grms. of sulphur are

burned, i.e.,  $\frac{71,080}{32} \times 832 = 1,848,000$  C.H.U. are liberated per hour at the burners when 832 lb. of sulphur are burned to  $\text{SO}_2$ .

(2) From  $\text{SO}_2$  burned to  $\text{SO}_3$ —

2 per cent. of total  $\text{SO}_2$ , i.e.,  $832 \times \frac{64}{32} \times .02 = 33.3$  lb.

$\text{SO}_2$  are converted to  $\text{SO}_3$  at the burners, giving 41.6 lb.  $\text{SO}_3$ .

$\text{SO}_2 + \text{O} = \text{SO}_3 + 20,820$  cal. (Berthelot).

$\therefore 20,820$  C.H.U. are liberated when 64 lb.  $\text{SO}_2$  are converted to  $\text{SO}_3$ .

Hence  $\frac{20,820}{64} \times 33.3 = 10,850$  C.H.U. are liberated when

33.3 lb.  $\text{SO}_2$  are converted to  $\text{SO}_3$  at burners.

Hence total heat generated at burners is (1) + (2),

$= 1,848,000 + 10,850$

$= 1,858,850$  C.H.U. per hour

*Heat removed or lost at burners.*— $\text{SO}_2$  forms 8.5 per cent. by volume of the burner gases. The density of  $\text{SO}_2$  compared to that of air is 2.26.

Hence  $\text{SO}_2$  percentage by weight is—

$$\frac{8.5 \times 2.26}{8.5 \times 2.26 + 91.5} = \frac{19.2}{110.7} = 17.3 \text{ per cent.}$$

There is, therefore, per hour, of burner gases—

$\text{SO}_2$  1,631 lb. specific heat at constant pressure, 0.154.

$\text{SO}_3$  41.6 lb. specific heat at constant pressure, 0.137.

Air.  $\frac{1631 \times 82.7}{17.3} = 7,800$  lb. specific heat at constant pressure, 0.243.

Moisture in air, 45 lb.; from crude sulphur, 5 lb.; total, 50 lb.

Specific heat of water vapour, 0.473; latent heat of evaporation, 537.

(Specific heats taken as far as possible for range 0–600° C.)

The temperature of the burner gases is about 595° C., atmospheric temperature is taken as 15° C.

Hence we have heat absorbed by burner gases is—

	C.H.U.
(1) By $\text{SO}_2 = 1631 \times 0.154 \times 580$	= 145,700
(2) By air = $7800 \times 0.243 \times 580$	= 1,099,300
(3) By $\text{SO}_3 = 41.6 \times 0.137 \times 580$	= 3,300
(4) By water vapour = $50 \times 0.473 \times 580$	= 13,700
(5) To evaporate 5 lb. water at 15° C. = $5 \times 622$	= 3,100
	<hr/>
	1,265,100

Eliminating heat required for volatilisation of moisture (5), we have heat required to produce a temperature rise of 1° C. over this interval (0° – 600° C.)

$$= \frac{1,265,100 - 3,100}{580} = \frac{1,262,000}{580} = 2,174 \text{ C.H.U.}$$

#### *Heat balance at burners.*

<i>Produced or received.</i>		<i>Removed or lost.</i>	
	C.H.U.		C.H.U.
1. Combustion of sulphur to $\text{SO}_2$	per hour. 1,848,000	1. Carried away by burner gases	per hour. 1,265,100
2. Conversion of $\text{SO}_2$ to $\text{SO}_3$	10,850	2. Radiated by brickwork, &c., &c.	593,750
	<hr/>		<hr/>
	1,858,850		1,858,850

Loss of heat through brickwork of burners = 593,750 C.H.U.

Total surface area of burners = approximately 2,000 square feet.

∴ Heat lost per square foot per hour = say, 300 C.H.U.

(This is a high figure and the burners have since been lagged.)

## Section 2.—Heater-cooler balance.

*Heat given up by burner gases.*—Burner gases enter at  $590^{\circ}\text{C}$ . and leave at  $276^{\circ} = 314^{\circ}\text{C}$ . fall. It has been shown in section 1 above that the heat required per hour to produce a temperature difference of  $1^{\circ}\text{C}$ . in the burner gases is 2,174 C.H.U.

$$\begin{aligned}\text{Hence heat given up by burner gases} &= 2,174 \times 314. \\ &= 682,600 \text{ C.H.U. per hour.}\end{aligned}$$

*Heat taken up by purified gases.*—Purified gases enter at  $191^{\circ}\text{C}$ . and leave at  $327^{\circ}\text{C}$ .; rise  $136^{\circ}\text{C}$ . The pure gas consists of the  $\text{SO}_2$  produced at the burners (1,631 lb. per hour) mixed with air to form a 5 per cent. mixture by volume.

$$\text{Weight proportion of } \text{SO}_2 = \frac{5 \times 2.26}{5 \times 2.26 + 95} = \frac{11.3}{106.3} = 10.38 \%$$

$$\text{Weight of air per hour} = \frac{1631 \times 89.62}{10.38} = 14,100 \text{ lb.}$$

$\therefore$  Heat taken up per hour, for a temperature rise of  $136^{\circ}\text{C}$ . is—

$$\begin{array}{rcl}\text{By } \text{SO}_2 & 1,631 \times 0.154 \times 136 & = 34,190 \\ \text{By air} & 14,100 \times 0.243 \times 136 & = 466,000 \\ \hline \text{Total} & & = 500,200\end{array}$$

From which it follows that the heat required per hour for a difference of  $1^{\circ}\text{C}$ . in these gases is  $\frac{500,200}{136} = 3,680 \text{ C.H.U.}$

*Heat balance at heater-cooler.*

	C.H.U. per hour.		C.H.U. per hour.
Heat given up by burner gases - - -	682,600	Heat absorbed by pure gases - - -	500,200
		Heat lost by radiation, &c. - - -	182,400
	<u>682,600</u>		<u>682,600</u>

$$\text{Thermal efficiency of heater cooler} = \frac{500,200}{6,826} = 73.4 \text{ per cent.}$$

Total surface of cast-iron pipes in heater cooler—

48 pipes of  $6\frac{1}{2}$  inches external diameter and 23 feet long.

$$\text{Surface} = 48 \times 23 \times \frac{6.5}{12} \times \frac{22}{7} = 1,880 \text{ square feet.}$$

$$\frac{500,200}{1,880} = 264 \text{ C.H.U. per square foot of cast-iron surface}$$

per hour.



Total area of brickwork of heater cooler—

1,200 square feet (top and  $3\frac{1}{2}$  sides).

∴ Heat lost per square foot per hour of brickwork

$$= \frac{682,600 - 500,200}{1,200} \\ = 152 \text{ C.H.U.}$$

### Section 3.—Sulphur dioxide coolers.

The burner gases are cooled from  $276^{\circ}$  to  $20^{\circ}$  C.; fall =  $256^{\circ}$  C. It was found above that the heat which must be abstracted per hour to produce a temperature difference of  $1^{\circ}$  C. is 2,174 C.H.U. Hence, heat removed at coolers =  $2,174 \times 256 = 554,500$  C.H.U.

The heat given up by condensation of steam and formation of  $\text{H}_2\text{SO}_4$ , &c., at this point is small, and is neglected.

### Section 4.—Heat-exchanger.

*Heat gained by purified gases.*—The purified  $\text{SO}_2$  gases enter at  $20^{\circ}$  C., and leave at  $194^{\circ}$  C. Rise,  $174^{\circ}$  C. It is seen from Section 2 above that the heat required per hour for a rise of  $1^{\circ}$  C. in these gases is 3,680 C.H.U. Hence—

Heat gained by purified gases =  $3,680 \times 174 = 640,500$  C.H.U.

*Heat given up by  $\text{SO}_3$  gases.*—The gases entering the converter consist of 1,631 lb.  $\text{SO}_2$  and 14,100 lb. air per hour. Assuming 96 per cent. conversion, the following gases leave the converter :—

	C.H.U.
65 lb. $\text{SO}_2$ of specific heat at constant pressure $0.154 =$	10
1,957 lb. $\text{SO}_3$ " " " " $0.137 =$	268
13,709 lb. air " " " " $0.243 =$	3,333
	<u>3,611</u>

The heat required per hour to produce a temperature change of  $1^{\circ}$  C. in these gases is therefore 3,611 C.H.U.; the gases enter the heat exchanger at  $420^{\circ}$  C. and leave at  $280^{\circ}$  C.; fall,  $140^{\circ}$  C. Hence the heat given out by  $\text{SO}_3$  gases =  $3,611 \times 140$   
= 506,000 C.H.U.

There is practically no loss from the heat exchangers, and the apparent gain is probably due to error in pyrometer.

The value for the heat exchanger is taken as the mean, 573,000 C.H.U.

External exchangers = 1,240 square feet.

∴ Thermal value of tubes =  $\frac{573,000}{1,240} = 460$  C.H.U. per square foot per hour.

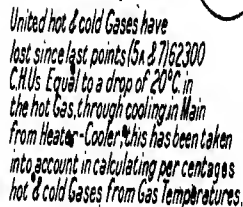


## UNIT 3. QUEEN'S FERRY.

Pounds crude Sulphur consumed per Burner per Hour = 75

1. Temperature of Gases
2. Weight & Composition of Gases passing per Hour
3. Heat carried by Gases, in Centigrade Heat Units, calculating from  $0^{\circ}\text{C}$ .

20% Cold Gas at 35°C. going to Converters } 100% losing 20°C due to cooling  
80% Hot Gas at 408°C " " " } by Gas Mains.



1. Heats of Reaction.  
 $S + O_2 = SO_2 + 71080 \text{ Cal.}$   
 $2SO_2 + O_2 = 2SO_3 + 41640 \text{ Cal.}$
2. Specific Heats at constant Pressure for temperature Ranges Involved.  
 $SO_2 = 0.154$  Air = 0.243.  
 $SO_3 = 0.137$  Water vapour = 0.473.
3. Weights of Material Involved.

116 Crude Sulphur contains Pure Sulphur 0.977 lb.  
Moisture 0.016 lb., this requires at Burners 8.16 lb. Air  
carrying 0.636 lb. Moisture. The Burner Gases contain  
11% by volume of  $\text{SO}_2$  & for 116 Crude Sulphur will  
consist in  $\text{SO}_2$  1.883 lb.  $\text{SO}_3$  0.078 lb. Water Vapour  
0.081 lb. Oxygen & Nitrogen taken as equivalent to Air  
for purposes of this calculation 6.832 lb. Total 8.879  
lbs After Purification, Gases for 116 Crude Sulphur  
will consist in  $\text{SO}_2$  1.883 lb. Air 15.14 lb.  
After Convection at 36.5%, Gases will consist in  $\text{SO}_2$   
2.278 lbs  $\text{SO}_3$  0.0667 lb. Air 14.63 lb.

4. Quantities of Heat Concerned for 1lb. Crude Sulphur:  
Heat involved at Burners 2213 Cal.  
Heat evolved at Converters 599 Cal.

5. Heat Required for Temperature Difference of  $1^{\circ}\text{C}$  per 1lb. Crude Sulphur Burned:-  
In Burner Gases 2588 CHU.  
In Purified SO<sub>2</sub> Gases 4381 CHU.  
In SO<sub>2</sub> Gases from Converters 4300 CHU.

Temperature changes due to Pressure variations not calculated or allowed for, as practically within Errors of determination of Temperatures by Pyrometers, as checked by crystallising Lead at 327°C.

FIG. 25.

**Section 5.—Converter balance.****(a) Gases entering Converter.**

These are at a temperature of  $330^{\circ}\text{C}$ ., and carry (see section 2 above)  
 $330 \times 3,680 \text{ C.H.U.} = 1,214,000 \text{ C.H.U.}$

**(b) Heat of Conversion.**

Assuming 96 per cent. conversion, 1,566 lb.  $\text{SO}_2$  are converted to  $\text{SO}_3$  per hour—

$$\begin{aligned} \text{Heat liberated (see Section 1)} &= \frac{20,820 \times 1,566}{64} \\ &= 510,000 \text{ C.H.U.} \end{aligned}$$

**(c) Gases leaving Converter.**

They are at a temperature of  $420^{\circ}$ , and carry therefore (see sec. 4)  $3,611 \times 420 = 1,516,000$ .

The balance, therefore, is—

**Heat brought in and produced.****Heat removed and lost.**

	C.H.U. per hour.		C.H.U. per hour.
By gases entering converter	1,214,000	By exit gases	1,516,000
By heat of reaction	510,000	Lost from converter	208,000
	<hr/> 1,724,000		<hr/> 1,724,000

The total surface presented by two converters is as follows:—

A cross-section near the top gives diameter 7 feet 6 inches + 9 inch brick + 18 inch Kieselguhr = 9 feet 9 inches; near the bottom, 7 feet 6 inches + 18 inch brick + 9 inch Kieselguhr = 9 feet 9 inches. Total height, 14 feet.

$$\begin{aligned} \therefore \text{Surface of brickwork} &= 9.75 + 3.14 \times 14 = 429 \\ \text{Area of cover } (9.75) \times .7854 &= 75 \end{aligned}$$

$$\begin{aligned} \text{Total exposed surface of 1 converter} &= 504 \\ \text{Total exposed surface of 2 converters} &= 1,008 \end{aligned}$$

$\therefore$  loss of heat per square foot per hour—

$$= \frac{208,000}{1,008} = 208 \text{ C.H.U.}$$

Fig. 25 gives a thermal efficiency chart of the working of one unit of the Grillo plant about a year after the above results were recorded and calculated.

### CALCULATIONS INVOLVED IN THE DESIGN OF THE PLANT

In the following pages are given from page 78 to page 93 calculations made before the erection of the plant to ascertain the quantity of heat which would have to be dealt with by the coolers in the Grillo absorption system, and from page 93 to page 101 another set of calculations to determine the size of cooler required for the absorption system in another plant.

Pages 102 to 111 comprise a report on the thermal effects in the absorption system at Queen's Ferry determined practically and calculated theoretically from first principles. Pages 111 to 119 comprise a similar report on the same portion of the plant at Avonmouth and a comparison of the results obtained there and at Queen's Ferry.

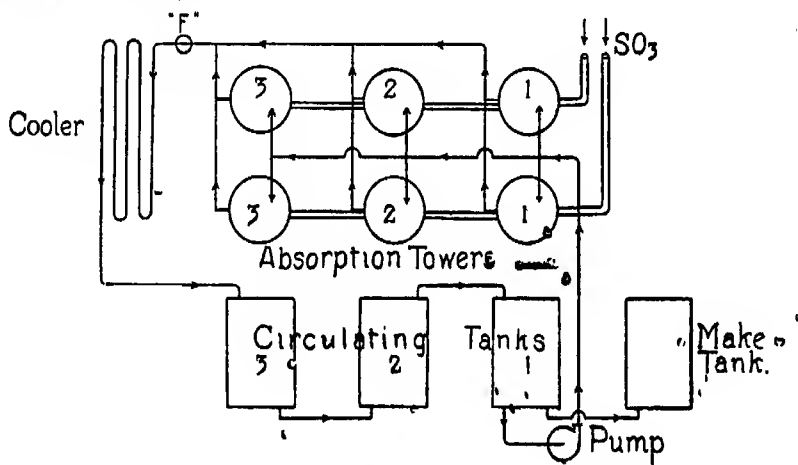
### CALCULATIONS FOR DETERMINING THE QUANTITY OF HEAT TO BE DEALT WITH BY THE COOLERS IN THE GRILLO ABSORPTION SYSTEM, ALSO THE QUANTITY OF ACID TO BE PUMPED OVER THE TOWERS

The following calculations are based on the assumption that the crude sulphur stoked into the burners is 97 per cent. pure whilst the conversion of  $\text{SO}_2$  to  $\text{SO}_3$  is 95 per cent.

$\text{SO}_3$  produced per 100 lb. of crude sulphur burned will therefore be :—

$$100 \times .97 \times \frac{80}{32} \times .95 = 231 \text{ lb.}$$

**98 per cent. acid production.**—Each unit of absorption plant consists of six absorbing towers with the necessary circulating acid tanks, pumps, pipes, coolers, &c. The strength of the circulating acid to all towers must be maintained at approximately 98 per cent., at which strength sulphuric acid has its greatest affinity for  $\text{SO}_3$ , whilst the feed acid or water is added to the system in its exact proportion to the  $\text{SO}_3$  to make 98 per cent. acid.



By similar calculations the following curve has been constructed in Fig. 27 :—

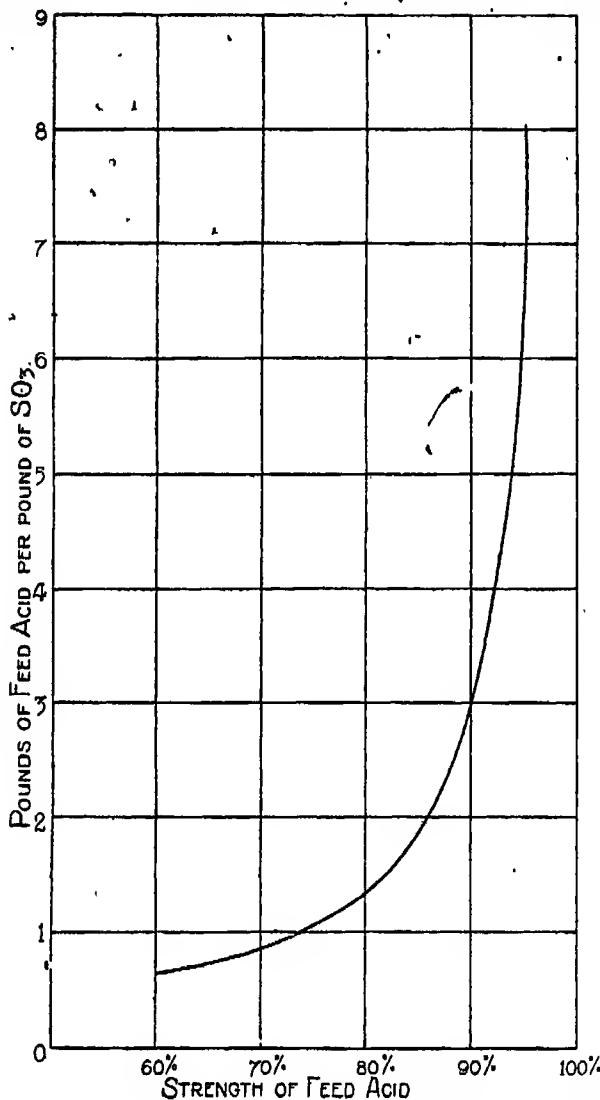


FIG. 27.

For each 100 lb. sulphur burned the amount of SO<sub>3</sub> produced = 231 lb. per hour.

∴ The total feed acid required per 100 lb. sulphur burned will be as follows :—

Table I.

Strength of feed acid per cent. H <sub>2</sub> SO <sub>4</sub>	Acid required per 100 lb. crude sulphur burned to produce 98 per cent. H <sub>2</sub> SO <sub>4</sub> lb.	Strength of feed acid per cent. H <sub>2</sub> SO <sub>4</sub>	Acid required per 100 lb. crude sulphur burned to produce 98 per cent. H <sub>2</sub> SO <sub>4</sub> lb.
0 (= water)	57.8	86	314
60	149	85	435
65	171	88	552
70	200	90	700
75	243	95	1,850

For water feed :—

98 per cent. acid = 80 per cent.  $\text{SO}_3$  + 20 per cent. water.

$\therefore$  water required per 231 lb.  $\text{SO}_3 = 231 \times \frac{20}{80}$

= 57.8 lb. per 100 lb. crude sulphur burned,

Heat produced during absorption per 100 lb. crude sulphur burned  
= 231 lb.  $\text{SO}_3$ .

When calculating the heat given out during absorption it will be assumed that 100 per cent. acid is being made, in which case the thermal equations

(1)  $\text{SO}_3 \text{ gas} \rightarrow \text{SO}_3 \text{ liq.} + 9,560 \text{ C.H.U.}$ , and

(2)  $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 21,320 \text{ C.H.U.}$  can be used.

These quantities of heat are by far the largest involved, and will be the only ones considered in these calculations.

(1) Heat of liquefaction of 231 lb. gaseous  $\text{SO}_3$

$$\frac{9560 \times 231}{80} = 27,600 \text{ C.H.U.}$$

(2) Heat of combination of 231 lb. liquid  $\text{SO}_3$

$$\text{with } \text{H}_2\text{O} \quad \frac{21,320 \times 231}{80} = 61,600 \text{ C.H.U.}$$

$$\text{Total} = \underline{\underline{89,200 \text{ C.H.U.}}}$$

or  $\frac{89,200}{231} = 386 \text{ C.H.U. per 1 lb. of } \text{SO}_3 \text{ gas combined with water.}$

The heat generated in the absorption towers will therefore be 89,200 C.H.U. per 100 lb. crude sulphur burned.

**Amount of acid to be pumped over towers.**—At approximately 98 per cent. strength sulphuric acid attains its maximum affinity, or absorbing power, for  $\text{SO}_3$ , and it is therefore essential that the circulating acid fed to the towers should be maintained at this strength. 98 per cent. acid, if kept fairly cool, has very little corrosive effect on cast iron or steel, but if the strength of the acid is allowed to rise above 99½ per cent., then the corrosive effect increases considerably. Should the strength rise above 99½ per cent. to, say, 1 or 2 per cent. oleum, then effect on either cast iron or steel becomes very marked, and pipes, pumps, towers, &c., will be ruined in a very short space of time.

It is therefore of the utmost importance that the 98 per cent. acid being fed to the towers should not increase in strength in the towers to above, say, 99¼ per cent., otherwise the depreciation and upkeep of the plant will be extremely high.

Now 1 lb. of 98 per cent. acid is composed of

$$0.8 \text{ lb. } \text{SO}_3 + 0.2 \text{ lb. } \text{H}_2\text{O}$$

and 1 lb. of 99.25 per cent. acid contains

$$\begin{aligned} &0.8102 \text{ lb. } \text{SO}_3 + 0.1898 \text{ lb. } \text{H}_2\text{O} \\ &= 0.8537 \text{ lb. } \text{SO}_3 + 0.2 \text{ lb. } \text{H}_2\text{O} \end{aligned}$$

but in 1 lb. of 98 per cent. acid there is already

0.8 lb.  $\text{SO}_3$ .  $\therefore \text{SO}_3$  to be added to 1 lb. of 98 per cent. acid to produce 99.25 per cent. acid =  $0.8537 - 0.8 = 0.0537$  lb.

or  $\frac{1}{0.0537} = 18.62$  lb. 98 per cent. acid per lb. of  $\text{SO}_3$  absorbed.

$\text{SO}_3$  evolved per 100 lb. crude sulphur burned = 231 lb.

$\therefore$  feed required to towers =  $231 \times 18.62$

= 4,300 lb. 98 per cent. acid per 100 lb. crude sulphur burned.

At Queen's Ferry and Gretna each unit is equipped with 12 sulphur burners, each of which is capable of burning up to 100 lb. of crude sulphur per hour, that is, each unit can burn 1,200 lb. per hour.

The amount of feed acid to the towers will then be as follows for various burner charges:—

Table 2.

Crude sulphur per burner per hour. lb.	Crude sulphur burned per unit per hour. lb.	98 per cent. circulating acid to towers per hour.			
		Pounds.	Tons.	Cu. ft.	Galls
30	360	15,480	6.91	135	831
40	480	20,640	9.21	179	1,105
50	600	25,800	11.50	224	1,390
60	720	30,960	13.83	269	1,670
70	840	26,120	16.11	314	1,960
75	900	38,700	17.28	336	2,090
80	960	41,280	18.44	359	2,210
85	1,020	43,860	19.60	382	2,370
95	1,080	46,440	20.76	404	2,500
95	1,140	49,020	21.90	426	2,650
100	1,200	51,600	23.00	447	2,780

Table No. 3 gives the weight of  $\text{SO}_3$  made and heat produced by absorption of various charges of sulphur burned.

Table 3.

Crude sulphur stoked per hour. lb.		$\text{SO}_3$ produced per Grillo unit per hour. lb.	Heat evolved during absorp- tion per unit per hour. C.H.U.
Per burner.	Per unit.		
30	360	832	321,000
40	480	1,116	428,000
50	600	1,380	535,000
60	720	1,662	642,000
70	840	1,940	740,000
75	900	2,080	803,000
80	960	2,220	856,000
85	1,020	2,360	910,000
90	1,080	2,490	964,000
95	1,140	2,630	1,016,000
100	1,200	2,770	1,070,000



The evolution of heat during absorption will raise the temperature of the circulating acid in its passage down the absorption tower, the rise in temperature being constant for all burner charges providing that the amount of acid passing down the towers is kept in its proper proportion to the charge as given in Table No. 2.

Examining the heat produced by 100 lb. charges and assuming that the whole of the heat is taken up by the circulating acid (that is, neglecting the heat imparted to the outgoing gases, and radiation). Table No. 2 gives 51,600 lb. of 98 per cent. acid passing and a heat evolution of 1,070,000 C.H.U. per hour.

Specific heat of 98 per cent. acid = 0.34

Then rise in temperature will be—

$$\frac{1,070,000}{51,600 \times 34} = 61.5^{\circ} \text{ C.}$$

If the temperature of the circulating acid in the tanks is maintained at 25° C., then the temperature of the acid from the towers at the entrance to the coolers will be 61.5 + 25 = 86.5° C.

#### *Acid Cooler.*

The cooler will be arranged on the evaporative principle and will consist of a long length of 6 inch internal diameter cast-iron pipe  $\frac{1}{8}$  inch thick.

The surrounding air temperature about the cooler will be assumed to be approximately 20° C.

When running 100 lb. charges the amount of acid to be cooled—

= 447 cubic feet per hour. (From Table 2.)

= 0.124 cubic foot per second.

Cross-sectional area of 6 inch pipe = 0.196 square foot.

$$\therefore \text{Velocity of flow} = \frac{0.124}{0.196} = 0.632 \text{ foot per second.}$$

(The available head is sufficient to give a velocity exceeding 0.632 foot per second.)

From Table 3 the heat to be absorbed by cooler is

= 1,070,000 C.H.U. per hour.

= 297 C.H.U. per second.

**Pumping equipment.**—Acid to be circulated over towers when burning 100 lb. charges.

= 447 cubic feet per hour.

= 0.1242 cubic foot per second. (From Table 2)

Height of lift including pipe friction, say = 36 feet.

If  $2\frac{1}{4}$  inch rising mains from pumps be used, then area of cross-section of pipe = 0.0272 square foot, and velocity of flow

$$= \frac{0.1242}{0.0272} = 4.56 \text{ feet per second.}$$



abstracted by the cooler before the acid returns to the tanks for further circulation round the towers.

It is evident, however, that if feed acid is continually entering the circulating system, and 98 per cent. acid is being continually made, that some arrangement must be made for passing the excess acid on to the oleum system where it can absorb a further amount of  $\text{SO}_3$  to produce the 20 per cent. oleum which is required.

The easiest way to accomplish this is to allow the excess 98 per cent. acid from tanks 2 and 3 continually to overflow into No. 1 tank, which contains the oleum for No. 1 tower circulation.

This method, however, has the serious disadvantage that the whole of the heat developed during the mixing of the 98 per cent. acid with the oleum takes place in the tank, and consequently the pumps have to deal with warm acid, which is, of course, bad practice. This, however, is not so great a disadvantage as the fact that warm oleum will be pumped to the top of the towers to absorb the incoming  $\text{SO}_3$ . Now the vapour tension of oleum increases very rapidly as its temperature rises, and consequently the higher the temperature of the oleum being fed to the towers the lower will be its power of absorbing the  $\text{SO}_3$ . The temperature of the feed will, therefore, have a marked effect on the amount of  $\text{SO}_3$  which will be absorbed to produce 20 per cent. oleum and the amount which will escape being absorbed in the No. 1 tower and pass on to Nos. 2 and 3 towers to produce 98 per cent. acid. This again has an effect on the strength of the feed acid which can be economically used; thus if reference is made to Table No. 6 it will be found that if 70 per cent. of the  $\text{SO}_3$  can be absorbed in the No. 1 towers, then feed acid of 93.7 per cent. strength can be economically employed, whereas if the percentage of absorption drops as low as 50 per cent. then the limiting strength of the feed acid drops to 84.2 per cent., the volume of oleum produced being in the proportion of 618.8 to 438.9 respectively. If the absorption plant be regarded as a concentrator, then the advantage of high absorption in the No. 1 tower is very marked, since with 70 per cent. absorption in No. 1 tower, 286 lb. of 90 per cent. acid can be concentrated to 20 per cent. oleum as against 195.5 lb. of the same acid if the absorption falls to 50 per cent.

It is obvious, therefore, that for good results from the plant, quite apart from the maintenance point of view, that the feed to the towers should be kept as cool as possible, and that either fresh feed acid or 98 per cent. acid from towers 2 and 3 should enter the oleum circulating system at some point other than the circulating tank, and as near to the inlet to the cooler as possible.

Referring to Fig. 28 the feed acid inlet to the 98 per cent. acid circulation is at point "F" and another inlet at "G" in the oleum circulation, and it would be an advantage therefore if the 98 per cent. make from No. 2 tank could be fed in at this opening.

If sufficient fall or head can be arranged for by placing the 98 per cent. acid tanks above the No. 1 tank, the overflow from No. 1 tank can gravitate to inlet "G." If, however, this is not possible, then the same end can be accomplished by taking a pipe from the 98 per cent.

acid pump delivery at "K" and tapping off the required amount of 98 per cent. acid to inlet "G," the exact amount of 98 per cent. acid being regulated by means of a constant flow acid meter, similar to those used for measurement of fresh feed acid.

**Amount of feed water or acid required.** 20 per cent. oleum = 85.3 per cent.  $\text{SO}_3$  + 14.7 per cent.  $\text{H}_2\text{O}$ , which is equivalent to 1 part  $\text{SO}_3$  + 0.1723 parts  $\text{H}_2\text{O}$ . 100 lb. of crude sulphur burned yields 231 lb. of  $\text{SO}_3$ .  $\therefore$  feed water required per 100 lb. crude sulphur burned = 39.6 lb.

Now suppose 70 per cent. acid for feed is used instead of water, then—

100 parts 20 per cent. oleum = 85.3 parts  $\text{SO}_3$  + 14.7 parts water.

100 parts 70 per cent. acid = 57 parts  $\text{SO}_3$  + 43 parts water.

$\text{SO}_3$  to be added to 43 parts water in 70 per cent. acid

$$= 43 \times \frac{85.3}{14.7} = 249 \text{ lb.}$$

But 100 lb. 70 per cent. acid contains 57 lb.  $\text{SO}_3$ .

$\therefore$   $\text{SO}_3$  to be added to 100 lb. 70 per cent. acid to form 20 per cent. oleum =  $249 - 57 = 192$  lb., which is equivalent to 0.521 lb. 70 per cent. acid per lb. of  $\text{SO}_3$ .

By similar calculation the accompanying curve (Fig. 29), showing the amount of feed of various strengths required per lb. of  $\text{SO}_3$  to form 20 per cent. oleum, has been plotted

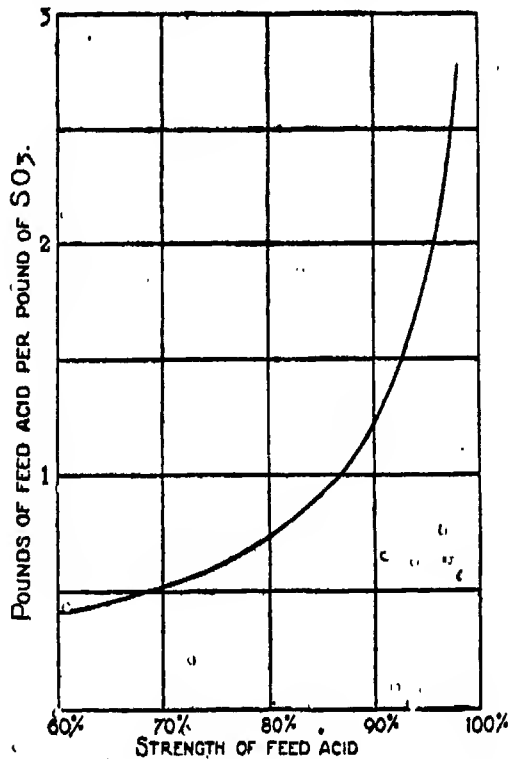


FIG. 29.

Each 100 lb. crude sulphur burned yields 231 lb. of  $\text{SO}_3$ , then the theoretical amount of feed acid of various strengths to produce oleum from gases from 100 lb. crude sulphur will be as given in Table No. 4.

TABLE 4.

Strength of feed acid per cent. $\text{H}_2\text{SO}_4$	Feed acid required per 100 lb. crude sulphur burned. lb.	20 per cent Oleum produced per 100 lb. crude sulphur burned. lb.
0 per cent. = Water	39.8	270.8
60 per cent.	96.0	327.0
65 per cent.	105.3	336.3
70 per cent.	120.4	351.4
75 per cent.	141.2	372.2
80 per cent.	170.0	401.0
*85 per cent.	214.7	445.7
*88 per cent.	254.0	485.0
*90 per cent.	287.0	518.0
*93 per cent.	361.0	591.0
*95 per cent.	434.0	665.0
*98 per cent.	636.0	861.0

Referring back to the flow of the plant, shown in Fig. 28, it is seen that in No. 1 tower the circulating acid is 20 per cent. oleum, whilst the feed consists of 98 per cent. acid, which overflows from No. 2 tank together with feed water or acid which enters at "G." It is obvious, therefore, that these two feeds must contain sufficient water to absorb the amount of  $\text{SO}_3$  which is taken up in No. 1 tower to produce 20 per cent. oleum, whilst the remaining feed which enters at "F" must be in its correct proportion to absorb the  $\text{SO}_3$  which passes out of No. 1 tower to form 98 per cent. acid for passing forward to No. 2 circulating tank.

The actual amount of  $\text{SO}_3$  taken up in the No. 1 tower has been shown to depend to a large extent on the coolness of the acid passed down the tower, the cooler the acid the greater being the absorption, but, generally, in a good running plant it is found that about 60 per cent. of the  $\text{SO}_3$  is absorbed in the first towers, the remaining 40 per cent. being caught in towers 2 and 3, or, more precisely, in No. 2 tower, since the amount of absorption in the last tower is necessarily small to ensure that practically no  $\text{SO}_3$  escapes absorption and passes to atmosphere.

The actual percentage of  $\text{SO}_3$  absorbed by the various towers, however, affects the distribution of the feed acid, and also the maximum strength of feed which can be employed. It therefore follows that the heat effect due to absorption in the two systems will vary with the temperature of the first or strong tower, and the amount of heat to be absorbed by the 98 per cent. acid cooler and the oleum cooler will vary according to the amount of  $\text{SO}_3$  absorbed to produce 98 per cent. acid, and oleum respectively.

\* See also Table No. 3 for values above 82.4 per cent. feed acid.

With regard to the feed distribution to points "F" and "G," it has been seen that the total amount, when considering water feed, is 39.8 lb. water per 100 lb. crude sulphur burned (Table No. 4), this amount being split up into two parts in proportion to the absorption in the towers, one part entering system at "G" and the remainder at "F."

Now suppose the absorption in No. 1 tower to be 60 per cent. of the  $\text{SO}_3$  produced, then

$$\begin{array}{rcl} \text{SO}_3 \text{ absorbed in No. 1 tower per 100 lb. crude sulphur} & & \\ \text{burned} & = & 139 \text{ lb.} \\ \text{SO}_3 \text{ absorbed in Nos. 2 and 3 towers per 100 lb. crude} & & \\ \text{sulphur burned} & = & 92 \text{ lb.} \\ & & \hline & & 231 \text{ lb.} \end{array}$$

Sufficient water is to be added at point "F" to combine with 92 lb.  $\text{SO}_3$  to form 98 per cent.  $\text{H}_2\text{SO}_4$   $\therefore$  water to be added

$$= 92 \times \frac{20}{80} = 23 \text{ lb.}$$

$$\begin{array}{l} \text{Total water to be added per unit per 100 lb. sulphur burned} \\ = 39.8 \text{ lb.} \end{array}$$

$$\therefore \text{water to be added at point "G"} = 39.8 - 23 = 16.6 \text{ lb.}$$

Now the feed to No. 1 tank consists of

(a) 16.8 lb. water to be raised to 20 per cent. oleum;

(b)  $92 + 23 = 115$  lb. 98 per cent. acid from No. 2 tank to be raised to 20 per cent. oleum.

Then  $\text{SO}_3$  require to make oleum from

$$(a) 16.8 \text{ lb. water} = 16.8 \times \frac{85.3}{14.7} = 97.6 \text{ lb. SO}_3$$

$$115 \text{ lb. 98 per cent. acid} = 92 \text{ lb. SO}_3 + 23 \text{ lb. H}_2\text{O}$$

$$\frac{85.3 \times 23}{14.7} = 133.4 \text{ lb SO}_3 \text{ required to form 20 per cent. oleum with the 23 lb of water.}$$

$$(b) \text{ but } \therefore 92.0 \text{ lb. SO}_3 \text{ are present in 115 lb. 98 per cent.}$$

$$\therefore 41.4 \text{ lb. SO}_3 \text{ must be added to 115 lb. 98 per cent. acid to form 20 per cent. oleum.}$$

Total  $\text{SO}_3$  required for (a) and (b)  $= 97.6 + 41.4 = 139$  lb., which from above is the exact amount available. It therefore follows that if a measuring device is used which will pass the exact amount of feed water or acid required per unit and a further instrument to split

this amount into two streams, one of which is exactly sufficient to make 98 per cent. acid in towers 2 and 3, then the remaining stream of feed acid will be the exact amount required to feed into No. 1 tower circulation to produce 20 per cent. oleum.

This holds true no matter what percentage of  $\text{SO}_3$  is absorbed in No. 1 or No. 2 towers.

The amount of  $\text{SO}_3$  to be absorbed in the two systems for various percentages of absorption is shown in the following table:—

TABLE 5.

Percentage of $\text{SO}_3$ absorbed in No. 1 or oleum towers.	$\text{SO}_3$ absorbed per 100 lb. crude sulphur burned.	
	In No. 1. Oleum towers.	Nos. 2 and 3 towers to produce 98 per cent. acid.
70 per cent.	162	69
68 per cent.	157	74
66 per cent.	152	79
64 per cent.	148	83
62 per cent.	143	88
60 per cent.	139	92
58 per cent.	134	97
56 per cent.	129	102
54 per cent.	125	106
52 per cent.	120	111
50 per cent.	115.5	115.5

The maximum amount of oleum which can be produced will occur when the feed to the oleum system consists solely of 98 per cent. acid, and it therefore follows that the amount of feed introduced must be exactly sufficient to form 20 per cent. oleum from the  $\text{SO}_3$  available for absorption in the tower.

The maximum strength of feed acid which can be employed without dilution will vary with the amount of  $\text{SO}_3$  to be absorbed in the strong towers, the greater the  $\text{SO}_3$  available in these towers the stronger the acid may be employed, since a greater volume of 98 per cent. acid can be handled in the oleum towers.

For various percentages of  $\text{SO}_3$  absorbed in the strong towers the amount of 98 per cent. acid can be calculated which can be dealt with, and finally the limiting strengths of feed which can be economically employed, that is, without the addition of water.

These values have been calculated for various amounts of  $\text{SO}_3$  absorbed in No. 1 tower from 50 to 70 per cent., the results being shown in Table No. 6.

TABLE 6.

Percentage of SO <sub>2</sub> absorbed in towers.		SO <sub>2</sub> available in towers 2 and 3 to form 98 per cent. acid per 100 lb. crude sulphur burned.	Limiting strength of feed acid which can be introduced without additional water.
No. 1. Per cent.	Nos. 2 and 3. Per cent.		
70	30	69	93.7
68	32	74	93.1
66	34	79	92.4
64	36	83	91.8
62	38	88	91.03
60	40	92	90.2
58	42	97	89.4
56	44	102	88.4
54	46	106	87.23
52	48	111	85.9
50	50	115.5	84.2

Now suppose it is desired to use 97 per cent. feed acid when the plant is running with an absorption of 60 per cent. in No. 1 towers, then, the amount of feed required can be calculated as follows. The available SO<sub>2</sub> is based on 100 lb. crude sulphur burned.

Then

$$\text{SO}_2 \text{ absorbed in No. 1 tower} = 139 \text{ lb.}$$

$$\begin{aligned} \text{From Table No. 4, 98 per cent. acid required to make oleum} \\ = 636 \text{ lb. per } 231 \text{ lb. SO}_2. \end{aligned}$$

$$\therefore 98 \text{ per cent. acid required to make oleum from } 139 \text{ lb. SO}_2$$

$$= 636 \times \frac{139}{231} = 382 \text{ lb.}$$

Now 98 per cent. acid consists of 80 per cent. SO<sub>2</sub> + 20 per cent. water, therefore 382 lb. 98 per cent. acid will consist of 305.6 lb. SO<sub>2</sub> + 76.4 lb. water, which of course must represent the composition of the feed entering the 98 per cent. circulation together with the SO<sub>2</sub> to be absorbed in towers 2 and 3.

$$\text{SO}_2 \text{ to be absorbed in towers 2 and 3} = 92 \text{ lb.}$$

$$\text{Then SO}_2 \text{ which must be in feed acid will be } 305.6 - 92 = 213.6 \text{ lb.}$$

From Table No. 7, 97 per cent. acid consists of

$$1 \text{ lb. SO}_2 + 0.2631 \text{ lb. water.}$$

$$\therefore 213.6 \text{ lb. of SO}_2 \text{ will be contained in}$$

$$\begin{aligned} [213.6 + (213.6 \times 0.2631)] &= (213.6 + 56.2 \text{ H}_2\text{O}) \\ &= 269.8 \text{ lb. 97 per cent. acid;} \end{aligned}$$



# CALCULATIONS : ABSORPTION

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but the water component required in the 98 per cent. feed to No. 1 tower was 76.4 lb.

∴ water to be added to 98 per cent. circulation will be .

$$76.4 - 56.2 = 20.2 \text{ lb.}$$

and the total feed required to towers 2 and 3 becomes

. 269.8 lb. of 97 per cent. acid + 20.2 lb. water.

By similar calculations the feed components for various strengths of feed acid above the limiting strength have been calculated and tabulated in Table 8.

TABLE 7.

Strength of feed acid per cent. $\text{H}_2\text{SO}_4$	100 parts contain		Ratio $\text{SO}_3$ to water.
	$\text{SO}_3$	$\text{H}_2\text{O}$	
60.0	48.978	51.082	I : I.0429
65.0	53.059	46.941	I : 0.8846
70.0	75.141	42.859	I : 0.7500
75.0	61.223	38.777	I : 0.6332
80.0	65.304	34.696	I : 0.5312
82.0	66.936	33.064	I : 0.4939
84.2	68.733	31.267	I : 0.4549
85.0	69.385	30.615	I : 0.4412
85.9	70.120	29.88	I : 0.4261
87.23	71.205	28.795	I : 0.4043
88.0	71.834	28.166	I : 0.3920
88.4	72.161	27.839	I : 0.3857
89.4	72.978	27.022	I : 0.3702
90.0	73.467	26.533	I : 0.3611
90.2	73.630	26.370	I : 0.3581
91.0	74.283	25.717	I : 0.3462
91.03	74.307	25.693	I : 0.3457
91.8	74.934	25.066	I : 0.3345
92.4	75.41	24.590	I : 0.3260
93.0	75.90	24.100	I : 0.3175
93.1	75.98	24.02	I : 0.3161
93.7	76.475	23.525	I : 0.3076
95.0	77.548	22.452	I : 0.2895
97.0	79.17	20.83	I : 0.2631

**Oleum cooler.**—The heat generated in the oleum circulation consists of two parts

- (1) The heat evolved by the formation of 100 per cent. acid from the water contained in the 98 per cent. acid entering the system, and the  $\text{SO}_3$  available,
- and
- (2) Heat of absorption of  $\text{SO}_3$  in 100 per cent. acid.

Of the two parts by far the greater amount of heat is developed by (1), and for the purpose of calculating the quantity of heat to be dealt with in the cooler, (2) can be neglected.

From Table No. 8 the maximum amount of 98 per cent. acid which can enter oleum system per 100 lb. crude sulphur burned = 456.8 lb.

98 per cent. acid consists of 98 per cent.  $\text{H}_2\text{SO}_4$  + 2 per cent.  $\text{H}_2\text{O}$   
 $\therefore$  water contained in 456.8 lb. 98 per cent. acid

$$= \frac{456.8 \times 2}{100} = 9.135 \text{ lb.}$$

Heat of formation of 100 per cent. acid from  $\text{SO}_3$  (gaseous) and water = 386 C.H.U. per lb. of  $\text{SO}_3$  absorbed.

100 per cent. acid consists of 81.6 per cent.  $\text{SO}_3$  + 18.4 per cent. water.

$$\therefore 9.136 \text{ lb. water will require } 81.6 \times \frac{9.136}{18.4}$$

$$= 40.5 \text{ lb. } \text{SO}_3 \text{ to make 100 per cent. acid.}$$

Then heat evolved will be—

$$40.5 \times 386 = 15,460 \text{ C.H.U. per 100 lb. crude sulphur burned.}$$

Maximum crude sulphur burned per unit per hour = 1,200 lb.; then heat to be absorbed by oleum cooler will be

$$15,460 \times 12 = 187,680 \text{ C.H.U. per hour.}$$

$$= 3,126 \text{ C.H.U. per minute.}$$

$$= 52 \text{ C.H.U. per second.}$$

**Amount of oleum pumped over towers.**—The feed to the oleum towers consists of 20 per cent. oleum, and sufficient must be put down the towers to ensure that the outlet from the towers does not exceed, say, 23 per cent. oleum.

$$\begin{aligned} 20 \text{ per cent. oleum} &= 80 \text{ per cent. } \text{H}_2\text{SO}_4 + 20 \text{ per cent. free } \text{SO}_3 \\ &= 85.3 \text{ per cent. } \text{SO}_3 + 14.7 \text{ per cent. water} \end{aligned}$$

$$\begin{aligned} 23 \text{ per cent. oleum} &= 77 \text{ per cent. } \text{H}_2\text{SO}_4 + 23 \text{ per cent. free } \text{SO}_3 \\ &= 85.8 \text{ per cent. } \text{SO}_3 + 14.2 \text{ per cent. water} \end{aligned}$$

$$\text{or } = 88.8 \text{ } \text{SO}_3 + 14.7 \text{ water.}$$

$\therefore$  to each 100 lb. of 20 per cent. oleum entering tower we must add  $88.8 - 85.3 = 3.5 \text{ lb. of } \text{SO}_3$  to produce 23 per cent. oleum.

Maximum  $\text{SO}_3$  to be absorbed will be when there are 100 lb. burner charges or 1,200 lb. sulphur burned per hour and 70 per cent. absorption in No. 1 tower, on which basis sufficient 20 per cent. oleum will be required in circulation to absorb  $162 \times 12 = 1,944$  lb.  $\text{SO}_3$  per hour to make 23 per cent. oleum.

As 3.3 lb.  $\text{SO}_3$  require 100 lb. 20 per cent. oleum

$$\therefore 1,944 \text{ lb. will require } \frac{1,944 \times 100}{3.3} = 59,000 \text{ lb. per hour}$$

$$= 26.3 \text{ tons per hour}$$

or 495 cubic feet per hour = 0.1375 cubic foot per second.

The rise in temperature of the circulating acid can now be calculated, since we know the weight of acid and the amount of heat which it must take up, whilst the specific heat of 20 per cent. oleum is approximately 0.339.

Then—

$$T_2 - T_1 \times 59,000 \text{ lb.} \times 0.339 = 187,680 \text{ C.H.U.}$$

$$T_2 - T_1 = \frac{187,680}{59,000 \times 0.339} = 9.4^\circ \text{ C.}$$

If the temperature of the cold acid is to be maintained at, say,  $25^\circ \text{ C.}$ , then the temperature of the hot acid will be  $34.4^\circ$ —

$$\text{Temperature of air surrounding cooler} = 19.5^\circ \text{ C.}$$

$$\text{Then difference in temperature of air and hot acid} = 14.9^\circ \text{ C.}$$

The cooler will consist of a long length of 5 inch internal diameter mild steel pipe, with walls  $\frac{1}{4}$  inch thick.

$$\text{Then area of 5 inch diameter pipe} = 0.136 \text{ square foot}$$

$$\text{and velocity of flow will be } \frac{0.1375}{0.136} = 1 \text{ foot per second.}$$

### SOME CALCULATIONS IN CONNECTION WITH H.M. FACTORY, AVONMOUTH

The plant will be arranged so that 98 per cent. acid or 20 per cent. oleum may be produced as desired.

These calculations have for their object to ascertain the size and capacity of acid coolers required, the volume of feed or circulating acid needed for good absorption, so that the lay-out of the absorption house may be altered to suit.

Each Grillo unit is credited with a capacity of 20 tons of  $\text{SO}_3$  per 24 hours, on the assumption that the overall efficiency from crude 97 per cent. sulphur burned will be 90 per cent.

The actual figures are—

$$9 \text{ tons (2,240 lb.) sulphur (crude), 97 per cent.}$$

$$= 8.73 \text{ tons pure sulphur.}$$

$$= 8.12 \text{ tons converted to } \text{SO}_3 \text{ at 93 per cent. conversion.}$$

$$= 8.04 \text{ tons absorbed at 99 per cent. absorption.}$$

$$= 20.1 \text{ tons } \text{SO}_3 \text{ produced.}$$

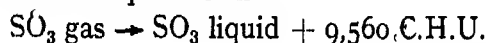
The converter system will handle more than this quantity, however; in fact, 25/30 tons of  $\text{SO}_3$  can be got from these units at the sacrifice of a little efficiency.

Therefore the absorption equipment must be proportioned to the output of, say, 25 tons  $\text{SO}_3$  daily, although the rating of the units will continue to be 20 tons  $\text{SO}_3$  daily.

*Calculation of the quantity of acid required for absorption of  $\text{SO}_2$  produced.*

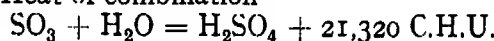
**Heat of absorption.**

(1) Heat of liquefaction—



$$\therefore \text{for 1 lb. SO}_3 \text{ gas } \frac{9,560}{80} = 119.5 \text{ C.H.U.}$$

(2) Heat of combination—



$$\therefore \text{for 1 lb. SO}_3 \text{ liquid } \frac{21,320}{80} = 266.5 \text{ C.H.U.}$$

$$\text{Total heat of absorption for 1 lb. SO}_3 \text{ gas} = \underline{386 \text{ C.H.U.}}$$

25 tons of  $\text{SO}_3$  therefore yield—

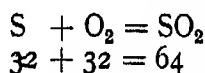
$$\begin{aligned} 25 \times 2240 \times 386 &= 21,620,000 \text{ C.H.U. per 24 hours per unit.} \\ &= 901,000 \text{ C.H.U. per 1 hour per unit.} \end{aligned}$$

**COMPOSITION OF GASES ENTERING AND LEAVING ABSORPTION TOWERS  
AND HEAT CONTENT OF SAME**

	$\text{N}_2$	$\text{O}_2$	$\text{SO}_2$	$\text{SO}_3$	Total Volume.
(A) Free air	79	21	—	—	100.0
(B) After burning sulphur to form $\text{SO}_2$ 5 per cent.	79	16	5	—	100.0
(C) After conversion to $\text{SO}_3$	79	13.5	—	5	97.5
(D) After absorption of all $\text{SO}_3$	79	13.5	—	—	92.5

Thus, 97.5 volumes of gas mixture entering absorption towers escape therefrom as 92.5 volumes, i.e., 100 volumes are reduced to 95 volumes.

The combustion of sulphur to  $\text{SO}_2$  yields gases (considered at NTP) as follows:—



$\therefore$  32 grams of sulphur burned to  $\text{SO}_2$  require 32 grams of oxygen or one molecular volume of oxygen = 22.4 litres, and yield one molecular volume of  $\text{SO}_2$ , i.e., 22.4 litres.

$$(1 \text{ lb.} = 454 \text{ grams.} \quad 1 \text{ cubic foot} = 28.32 \text{ litres.})$$

Therefore 1 lb. of sulphur yields—

$$\frac{22.4 \times 454}{32 \times 28.32} = 11.21 \text{ cubic feet } \text{SO}_2$$

and as this must represent not more than 5 per cent. of the gas mixture leaving the burners, we have :—

$$11.21 \times 20 = 224.20 \text{ cubic feet of atmospheric air per lb. of sulphur burned.}$$

For each lb. of sulphur burned the gases leaving the burner will be

	Cu. ft.	Lb.
<i>Nitrogen</i> ( $224.2 \times 79 \text{ per cent.}$ )	$= 177.12$	$= 13.82$
<i>Oxygen</i> ( $224.2 \times 16 \text{ per cent.}$ )	$= 35.87$	$= 3.19$
<i>SO<sub>2</sub></i> ( $224.2 \times 5 \text{ per cent.}$ )	$= 11.21$	$= 2.00$
<b>Total</b>	<b><u><u>224.20</u></u></b>	<b><u><u>19.01</u></u></b>

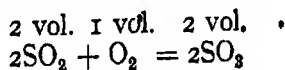
$$\text{N}_2 = \frac{22.4}{28} \times \frac{454}{28.83} = 12.82 \text{ cubic feet per lb.}$$

$$\text{O}_2 = \frac{22.4}{32} \times \frac{454}{28.33} = 11.21 \text{ cubic feet per lb.}$$

$$\text{SO}_2 = \frac{22.4}{64} \times \frac{454}{28.33} = 5.61 \text{ cubic feet per lb.}$$

$$\text{SO}_3 = \frac{22.4}{80} \times \frac{454}{28.33} = 4.485 \text{ cubic feet per lb.}$$

**Conversion to SO<sub>3</sub>.**—When these gases pass through the platinum converters the SO<sub>2</sub> is converted to SO<sub>3</sub> thus :—



and the contraction in volume indicated on page 94 takes place, namely, the 16 volumes of free oxygen suffer decrease to 13½ volumes, whilst the SO<sub>3</sub> formed occupies the same volume as the original SO<sub>2</sub>.

The gases actually entering the absorption towers (considered as at NTP) will then become per lb. sulphur burned :—

$$\text{Nitrogen} \quad \quad \quad = 177.12 \text{ cubic feet.}$$

$$\text{Oxygen} \quad \frac{35.87 \times 13.5}{16} = 30.25 \quad "$$

$$\text{SO}_3 \quad \quad \quad = 11.21 \quad "$$

$$\text{Total} = \underline{\underline{218.58}} \text{ cubic feet per lb. sulphur burned at } 100 \text{ per cent. conversion.}$$

As these gases enter absorbing towers at 50° C. and leave at 25° C., their volume becomes :—

	Entering tower.	Leaving tower.
Nitrogen, cubic feet	- 209.5	193.40
Oxygen, cubic feet	- 35.8	33.0
SO <sub>3</sub> , cubic feet	- 13.3	12.34
	<u>258.6</u>	<u>238.74</u>

Volume and weight of gases entering tower. 25 tons SO<sub>3</sub>, assuming 93 per cent. conversion, would be equivalent to 10.75 tons sulphur (as pure) burned per 24 hours.

Or—

$$\frac{10.75 \times 2240}{24} = 1,003 \text{ lb. sulphur per hour.}$$

Say, 1,000 lb. sulphur per hour.

The weight of the several gases is as follows :—

$$\text{Nitrogen } \frac{177.12}{12.8 \text{ cubic feet}} = 13.82 \text{ lb. N}_2$$

$$\text{Oxygen } \frac{30.25}{11.21 \text{ cubic feet}} = 2.7 \text{ lb. O}_2$$

$$\text{SO}_3 \quad \frac{11.21}{4.480} = 2.5 \text{ lb. SO}_3$$

$$\text{Total} = \frac{19.02 \text{ lb. gas mixture per lb. sulphur burned.}}$$

Specific heat gases (at constant pressure).

Taking nitrogen at 0.2438

Taking oxygen at 0.2175

Taking SO<sub>3</sub> at 0.1370

Volume of 98 per cent. absorbing acid required.—The SO<sub>3</sub> is most readily absorbed by 98 per cent. sulphuric acid, and it is desirable to keep the strength of the acid as nearly as possible to this figure.

Acid of 99½ per cent. to 103 per cent. H<sub>2</sub>SO<sub>4</sub> is extremely corrosive and quickly destroys steel, and at the same time is very likely to crack or disintegrate cast iron—due probably to dissolved SO<sub>3</sub> which penetrates the cast-iron and forms sulphate.

It is, therefore, the practice to keep the strength of the absorbing acid at 98 per cent. entering, and not more than 99½ per cent. leaving the absorbers.

Quantity of acid required to absorb 25 tons of SO<sub>3</sub> daily would be :—

$$25 \text{ tons SO}_3 \approx 30.62 \text{ H}_2\text{SO}_4 = 30.78 \text{ tons } 99\frac{1}{2} \text{ per cent. sulphuric acid.}$$

$$\therefore 5.78 \text{ tons H}_2\text{O are taken up by the SO}_3$$

100 tons of 98 per cent. feed acid would yield :—

98½ tons of 99½ per cent. acid, so that—

1.5 tons water would be available for absorbing the SO<sub>3</sub> per 100 tons 98 per cent. feed acid.

$$\therefore \frac{5.78 \times 100}{1.5} = 385.3 \text{ tons of 98 per cent. acid must be fed into towers per 24 hours.}$$

The output of the towers will then be :—

	Tons.
Feed acid . . . . .	385.3
SO <sub>3</sub> . . . . .	25.0
	<hr/>
	410.3 of 99½ per cent. sulphuric acid.

Therefore, one Grillo unit producing at the rate of 25 tons SO<sub>3</sub> daily, would require daily 385.3 tons of 98 per cent. feed acid, and on this basis, the pumping equipment should be calculated.

• **Heat balance of absorption system of one Grillo unit.**—From the data developed in foregoing paragraphs there is :—

*Entering towers per hour on basis 25 tons SO<sub>3</sub> daily.*—Equal to 1,000 lb. sulphur per hour at 93 per cent. conversion.

- Assume acid to enter absorption towers at 20° C.
- Assume gases to enter absorption towers at 60° C.
- Assume gases to leave tower at 20° C.

(This figure is purposely taken instead of 25° C. as mentioned on page 96 in order to make the case more difficult.)

	C.H.U. per hour.
Nitrogen 1,000 × 13.82 lb. × 0.2438 sp. ht. × 60° C. =	202,200
Oxygen 1,000 × 2.7 × 0.2175 × 60° C. =	35,220
SO <sub>3</sub> 1,000 × 2.5 × 0.1370 × 60° C. =	20,550
Absorbing acid $\frac{385.3 \times 2,240}{(24 \text{ hours})} \times 0.357 \times 20^\circ \text{C.} =$	256,761
	<hr/>
	514,731

Add heat of reaction—

$$\frac{(25 \text{ tons SO}_3 \times 2,240)}{24 \text{ hours}} \times 386 \text{ C.H.U.} = 901,000$$

Total C.H.U. entering tower + heat of reaction

$$\text{Total} \quad \text{---} \quad \text{(A)} \quad \underline{1,415,731}$$

Heat contained in gases leaving towers—

$$\text{Nitrogen } 1,000 \times 13.83 \text{ lb.} \times 0.2438 \times 20^\circ \text{C.} = 67,540$$

$$\text{Oxygen } 1,000 \times 2.7 \text{ lb.} \times 0.2175 \times 20^\circ \text{C.} = 11,740$$

$$\text{Total} \quad \text{---} \quad \text{(B)} \quad \underline{79,280}$$

Deduct total (B) from total (A) to determine heat conveyed away from towers by the 385.3 tons of feed acid + the 25 tons  $\text{SO}_3$  absorbed—

Total (A)	-	-	-	-	-	C.H.U.
Total (B)	-	-	-	-	-	1,415,731
						<u>79,280</u>
Difference (C)	-	-	-	-	-	<u>1,336,451</u>

*Acid leaving tower per 24 hours—*

						Tons.
Feed acid	-	-	-	-	-	385.3
$\text{SO}_3$ absorbed	-	-	-	-	-	<u>25.0</u>
Total 99½ per cent. acid	-	-	-	-	-	<u>410.3</u>

Then total (C) represents the number of C.H.U. which must be removed from the towers per hour by the acid.

$$\frac{1,336,451}{\frac{410.3 \times 2,240 \times 0.357}{24} \text{ (specific heat of 99½ per cent. sulphuric acid)}}$$

= 97.8° C., temperature of acid entering cooler.

(3) Heat to be eliminated per hour by coolers :—

$$\begin{array}{l} \text{Acid entering coolers—} \quad \text{C.H.U.} \\ \frac{410.3 \times 2240 \times 0.357 \times 97.8^\circ \text{C.}}{24 \text{ hours}} = 1,336,450 \end{array}$$

$$\begin{array}{l} \text{Acid leaving coolers—} \\ \frac{410.3 \times 2240 \times 0.357 \times 20^\circ \text{C.}}{24 \text{ hours}} = 273,200 \end{array}$$

$$\begin{array}{l} \text{Difference is the quantity of heat} \\ \text{to be eliminated per hour} \quad - \quad \underline{1,063,250} \end{array}$$

*Cooling surface required.*—Authorities vary as to the rate of heat exchange as between acid and cooling water through the medium of cast iron, and in default of better information the following figures, which are in substantial agreement with practice in acids factories, are assumed :—

One square foot of cast-iron 0.5 inch in thickness will pass per hour when the temperatures are respectively 77° C. and 20° C., 14 C.H.U. per degree.

We then have—

$$\frac{1,063,250}{14 \times (97.8 - 20)} = 975 \text{ square feet of surface required.}$$



Capacity of  $SO_3$  cooler.—25 tons  $SO_3$  per 24 hours.  
= 1,000 lbs. sulphur per burner.

1 lb. sulphur burned yields—

Nitrogen	-	-	-	177.12 cubic feet	} At NTP
Oxygen	-	-	-	35.57 cubic feet	
$SO_2$	-	-	-	11.21 cubic feet	
				<hr/> 224.20	

After passing converter these become—

Nitrogen	-	-	-	177.12 cubic feet	} At NTP
Oxygen	-	-	-	30.25 cubic feet	
$SO_3$	-	-	-	11.21 cubic feet	
				<hr/> 218.58	

The cold  $SO_2$  leaves blowers at, say,  $20^\circ$  C. and enters heat-exchanger, where it passes through tubes heated by  $SO_3$  from converters at, say,  $400^\circ$  C., thus the  $SO_2$  becomes heated at the expense of the  $SO_3$ , which becomes cooled.

The specific heat of the two gas mixtures is substantially the same, so that something approaching equilibrium of condition may be safely assumed in respect to temperature to be attained. (This assumption is made to obviate more or less unreliable calculations *re* heat transference through tubes, &c., of exchanger.)

The following conditions are assumed:—

Enters exchanger.	Leaves exchanger.
$SO_3$ gas $400^\circ$ C.	$\therefore \frac{400 + 20}{2} = 210^\circ$ C.
$SO_2$ gas $20^\circ$ C.	$\therefore \frac{400 + 20}{2} = 210^\circ$ C.

All data necessary are now available to enable the quantity of heat contained in the gases leaving the heat-exchanger to be calculated, from which can be deduced the quantity which must be removed in the  $SO_3$  coolers.

*C.H.U. contained in the  $SO_2$  gas entering the heat-exchanger.*

(Weights of gases corresponding to the volumes per 'lb. sulphur burned are taken from page 95.)

Enter $SO_2$ gas—	C.H.U.
Nitrogen $1000 \times 13.82 \times 0.2438 \times 20^\circ$ C.	= 67,400
Oxygen $1000 \times 3.19 \times 0.2175 \times 20^\circ$ C.	= 13,880
$SO_2$ $1000 \times 2.0 \times 0.154 \times 20^\circ$ C.	= 6,260
	<hr/> 87,440

			C.H.U.
SO <sub>3</sub> gas—			
Nitrogen	1000 × 13.82 × 0.2438 × 400° C. =	1,348,000	
Oxygen	1000 × 2.7 × 0.2175 × 400° C. =	235,000	
SO <sub>3</sub>	1000 × 2.5 × 0.1370 × 400° C. =	137,000	
			<u>1,720,000</u>
			<u>1,807,440</u>
Leave SO <sub>2</sub> gas—			
Nitrogen	1000 × 13.82 × 0.2438 × 210° C. =	708,000	
Oxygen	1000 × 3.19 × 0.2175 × 210° C. =	145,700	
SO <sub>2</sub>	1000 × 2.0 × 0.154 × 210° C. =	64,700	
			<u>918,400</u>
SO <sub>3</sub> gas—			
Nitrogen	1000 × 13.82 × 0.2438 × 210° C. =	708,000	
Oxygen	1000 × 2.7 × 0.2175 × 210° C. =	123,400	
SO <sub>3</sub>	1000 × 2.5 × 0.1270 × 210° C. =	71,900	
			<u>903,300</u>
Total C.H.U.			<u>1,821,700</u>

Thus the gases leaving the heat-exchanger and entering the SO<sub>3</sub> cooler (SO<sub>3</sub> cooler assumed to include the 10 inch pipe) contain

903,300 C.H.U. per hour.

The gases entering the absorbers at 60° C. contain, from page 97

Nitrogen	-	-	202,200 C.H.U.
Oxygen	-	-	35,220 "
SO <sub>3</sub>	-	-	20,550 "
			<u>257,970</u> "

Therefore  $903,300 - 257,970 = 645,300$  C.H.U. must be removed per hour from the gases.

The 10 inch steel pipe from the heat-exchanger to the SO<sub>3</sub> cooler may be taken as  $2 \times 120$  feet long (as there are two heat-exchangers and two pipes).

External diameter of this pipe,  $10\frac{3}{4}$  inches.

Surface of 1 foot length

$$\frac{10.75 \times 3.1416}{12} = 2.814 \text{ square feet.}$$

$$2.81 \times 240 = 675$$

Headers 94

$$\text{Total surface} = \underline{769} \text{ square feet.}$$

Air Cooling.

Temperature of SO <sub>3</sub>	-	210°
Temperature of air	-	20°

As the temperature will not remain constant throughout, the mean temperature difference will be taken as

$$\begin{array}{rcl} \text{Leaving exchanger} & : & - 210^{\circ} \\ \text{Entering absorbers} & - & - 60^{\circ} \end{array}$$

$$\text{Mean temperature } \frac{210 + 60}{2} = 135^{\circ}$$

$$\text{Temperature of air} \quad - \quad - 20^{\circ}$$

$$\therefore \text{Mean temperature difference } 135 - 20 = 115^{\circ}$$

Radiation loss per hour by Newton's law

$$115 \times 2.81 \times 0.64 = 206 \text{ C.H.U.}$$

(Factor for temperature difference  $115^{\circ}$  and air temperature  $20^{\circ}$  = 0.64).

Developing this in accordance with Dulong's law (factor for temperature difference  $115^{\circ}$  and air temperature  $20^{\circ}$  = 1.79)

$$206 \times 1.79 = 369 \text{ C.H.U. total loss by radiation.}$$

Convection loss (factor is 0.478 C.H.U. per square foot)

$$115 \times 2.81 \times 0.478 = 154.5 \text{ C.H.U.}$$

To conform to Dulong's law (factor 1.67)

$$154.5 \times 1.67 = 258 \text{ C.H.U.}$$

total loss by convection per hour per foot run.

Therefore total lost by radiation and convection becomes

$$\begin{array}{rcl} \text{Radiation} & 369 \\ \text{Convection} & 258 \\ \hline \end{array}$$

$$\text{Total } \underline{627} \text{ C.H.U. per hour per foot run.}$$

Surface of pipe per foot run is 2.81 square feet.

$$\therefore \frac{627}{2.81} = 223 \text{ C.H.U. per hour per square foot of surface for conditions stated.}$$

Cooling surfaces needed in order to eliminate by air cooling the heat contained in the gases produced by the combustion of 1,000 lb. of sulphur per hour, after same have left heat-exchanger:—

Heat units to be eliminated (page 100), 645,300 C.H.U.

Heat lost by radiation and convection per hour per square foot for above conditions per square foot, 223 C.H.U.

$$\therefore \frac{645,300}{223} = 2,893 \text{ square feet of cooling surface required.}$$

Surface available in 10 inch pipe and headers, 769 square feet.

Total surface to be provided as 6 inch pipes, as coolers, 2,124 square feet.

6 inch internal diameter = 6.5 inch external diameter.

$$\therefore \frac{6.5 \times 3.1416}{12} = 1.70 \text{ square feet per foot run.}$$

$$\therefore \frac{2124}{1.7} = 1,250 \text{ feet of 6 inch pipe required for cooler.}$$

### ABSORPTION SYSTEM—QUEEN'S FERRY GRILLO PLANT

In the following, the thermal effects in the Grillo absorption systems are determined practically and calculated theoretically from first principles.

The practical results are shown on Fig. 30 and the theoretical values appear on Fig. 31.

The scales are the same in both prints, and the discrepancies in the practical figures are probably due to the impossibility of measuring accurately all the thermal effects.

**Heat effects in absorption system.**—In the accompanying table, the results of several experimental runs on oleum and 98 per cent. units are given, showing the temperatures of the gases and acids at different parts of the circulation system, and the amounts of heat involved for varying sulphur charges.

The cooler surfaces were found by actual measurement to be 272 feet for the oleum cooler, and 1,212 feet for the standard cooler.

In some cases the acids entering and leaving the towers were analysed, but the absorption calculated from these were figures divergent from those indicated by theory.

One of the most difficult parts of the work was the accurate estimation of the amount of acid thrown by the pumps; the throws found are the most accurate that could be obtained under the conditions.

The measurement of the feed acid is a source of error; in no case was it found to correspond with the theoretical amount, being more than double in one case. The units appear to oscillate between limits, and are generally found to be either too strong or too weak.

The heat given out by the mixing of the returns from the towers and the incoming feed acid is somewhat uncertain, as the temperature of mixing is taken within a very short distance of the spot where the acids meet; it is probable that complete mixing is only obtained further along in the system, so that a low figure is obtained for this quantity.

The figure for radiation was taken by the heat rise in a quantity of sulphuric acid, contained in a narrow lead box of 1 square foot surface, placed within an inch or so of the surface of an oleum tower, in unit time (1 hour).

The heat given to the acid came to nearly 5 per cent. of the total heat measured, and this figure was taken as a standard correction; this correction, in the case of the 98 per cent. unit, must be higher than this figure, since the heat evolution is greater and the temperatures of the surfaces of the towers higher.

The loss of heat in the last two towers has, in each case, been neglected.

The specific heat of acids over 100 per cent.  $H_2SO_4$  has been taken as 0.34, and acids below 100 per cent. as 0.35.

See table on following page.

H. M. FACTORY QUEEN'S FERRY - GRILLO OLEUM PLANT.

H. M. FACTORY QUEEN'S FERRY - GRILLO OLEUM PLANT.

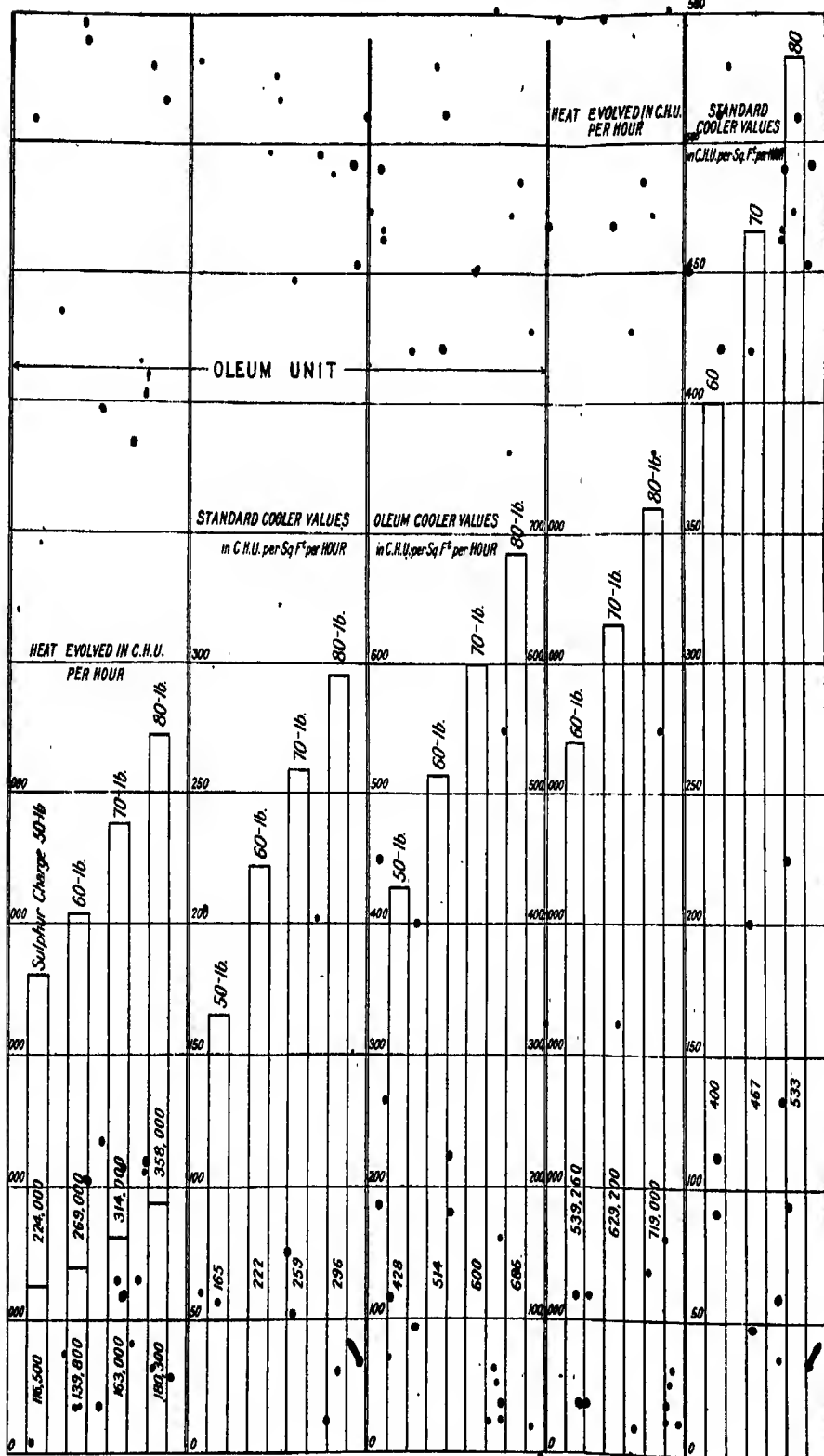
FIG. 30.

Malby & Sons Lith.



## HEAT EFFECTS IN ABSORPTION SYSTEM.

-98-99% H<sub>2</sub>SO<sub>4</sub> UNIT



**F-1 G' 31.**





HEAT EFFECTS IN ABSORPTION SYSTEM  
Table No. 1.

No. of Expt.	Date.	Sulphur charge lb./hr.	Gas temp entering towers		Acid Temperatures.				Heat evolved in C.H.U. front back systems.	Total 5 % radiation.	Cooler values C.H.U./ft./hr.																
			1 and 4.	2 and 5.	3 and 6.	Towers 1 and 4		Towers 2 and 5			Towers 3 and 6		Oileum Cooler	Standard Cooler													
						to	from	to			from	to			from												
																to	from	to	from	to	from						
1	19/6	50	57	51	33	°	°	48	64	°	°	34	31	°	°	64	49	°	°	56	35	°	°	140,530	354	453	—
2	22/6	60	56	54	35	°	°	52	60	°	°	33	32	°	°	66	54	°	°	55	34	°	°	196,890	290	144	500
3	26/6	70	65	57	42	°	°	55	73	°	°	40	38	°	°	73	59	°	°	67	42	°	°	119,060	328	301	214
4	27/6	80	62	56	36	°	°	51	71	°	°	39	34	°	°	71	53	°	°	63	41	°	°	194,090	810	146	—
																								137,860	413	346	—
																								255,970	520	179	—
																								148,670	411	445	—
																								243,490	770	130	—

Table No. 2.

No. of Expt.	Date.	Unit.	Sulphur charge lb./hr.	Gas temp. entering towers			Acid Temperatures.						Heat evolved — 5 % per radiation C.H.U. per hr.	Cooler (standard) in C.H.U./ft./hr.	Remarks.			
				1 and 4.	2 and 5.	3 and 6.	Towers 1 and 4		Towers 2 and 5		Towers 3 and 6					Standard Cooler		
							to	from	to	from	to	from				to	from	
5	27/6	4	60	54	57	39	43	95	43	50	43	41	60	44	400	365,870	Feed to 1st two towers reduced to thin stream (420 lb. per hour in each tower).	
6	28/6	4	70	50	91	43	44	67	48	103	48	40	72	50	—	208	381,730	
7	28/6	4	80	58	84	44	46	75	47	84	47	43	71	48	—	260	444,000	

**Calculation of heat evolved in absorption system.** Oleum units.—Six absorption towers are arranged in two parallel groups of three towers in series.

Acid of approximately 99 per cent. strength is fed over the back four towers, and acid of 105 per cent. strength is pumped over the front pair of towers.

The feed acid may be of any strength, as it is blended with the acid issuing from the back towers to make 99 per cent. acid—the excess of 99 per cent. acid overflows continuously and mixes with the strong oleum issuing from the front pair of towers to give 22 per cent. oleum which is pumped over the two strong towers—the excess running off to storage.

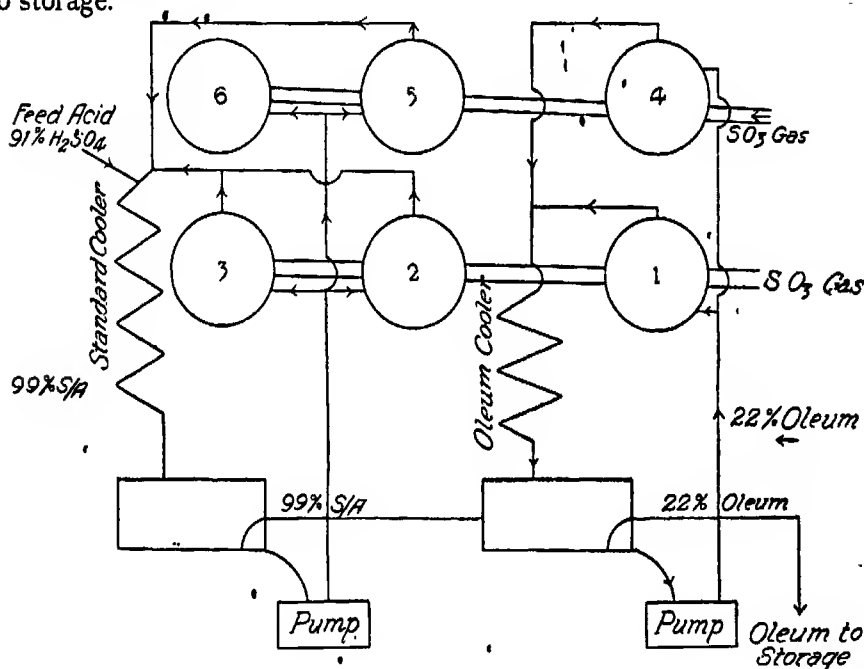


FIG. 32.

There are practically two systems :—

**System A** produces 98.5 to 99.5 per cent. sulphuric acid by combining  $SO_3$  with 91 per cent. feed acid—the heat of the combination being removed in the acid cooler.

**System B** is fed with the 99 per cent. acid made in system A and absorbs a certain part of the total  $SO_3$  to make 22 per cent. oleum, which is the final product.

**Calculation of heat evolved in Systems A and B when making 22 per cent. oleum and burning 60 lb. sulphur per burner hour.**

*Physical Data.*

Feed acid S/A	-	-	91.4 per cent. $H_2SO_4$
Acid forwarding from A to B	-	-	99.5 per cent. $H_2SO_4$
Acid produced in B	-	-	105 per cent. $H_2SO_4$

Sulphur burned = 720 lb. per hour (98.5 per cent. purity).

Pure sulphur = 709 lb. per hour.

Gases to towers 1 and 4 = 56° C. } Fall in temperature = 2° C.  
 Gases from towers 1 and 4 = 54° C. }  
 Gases to towers 2 and 5 = 54° C. } Fall in temperature = 20° C.  
 Gases to exit = 34° C. }

#### Calculations.

(A) Feed acid per hour = 2,056 lb. } SO<sub>3</sub> absorbed = 722 lb.  
 99.5 per cent. acid produced = 2,778 lb. }

(B) 105 per cent. acid produced = 3,678 lb. SO<sub>3</sub> absorbed = 909 lb.

#### Thermal System "A."

- (1) Condensation of gaseous to liquid SO<sub>3</sub> (positive).
- (2) Resolution of feed acid into 99.5 per cent. acid and water (negative).
- (3) Solution of liquid SO<sub>3</sub> in part of the resolved water to form monohydrate.
- (4) Dilution of monohydrate thus formed to yield 99.5 per cent. acid.
- (5) Heat given up by converter gases.

#### Determination of factor (1).

SO<sub>3</sub> gaseous = SO<sub>3</sub> liquid + 9,560\* C.H.U.  
 80 lb

$$\therefore 722 \text{ lb.} = \frac{9560 \times 722}{80} = 86,280 \text{ C.H.U.}$$

#### Determination of factor No. (2).

Imagine feed acid (2,056 lb.) split up into 99.5 per cent. acid and water. This will require a quantity of heat equal and opposite to that given out when 2,056 lb. of feed acid is formed by dilution of 99.5 per cent. acid.

The curve showing the relation between dilution of H<sub>2</sub>SO<sub>4</sub> and the heat evolved is a rectangular hyperbola, which can be represented by the function—

$$\frac{\text{H}_2\text{SO}_4, n\text{H}_2\text{O}}{98 \text{ lb.}} = \frac{n \times 17,860}{n + 1.7983}$$

where  $n$  = number of lb. molecules of water.

For 99.5 per cent. acid—

$$n = \frac{0.5 \times 98}{99.5 + 1.8} = 0.0274$$

using this value for  $n$  in above formula.

\* This figure is got as follows :—

- |                         |                  |   |                      |                                   |
|-------------------------|------------------|---|----------------------|-----------------------------------|
| (1) SO <sub>3</sub> gas | + Q              | = | SO <sub>3</sub> gas. | + 22,600 cal. (Berthelot).        |
| (2) S                   | + O <sub>2</sub> | = | SO <sub>2</sub> gas. | + 71,080 " (Thomsen).             |
| (3) S                   | + O <sub>3</sub> | = | SO <sub>3</sub> gas. | + (22,600 + 71,080) = 93,680 cal. |
| (4) S                   | + O <sub>3</sub> | = | SO <sub>3</sub> liq. | + 103,240 cal. (Thomsen).         |
| (5) SO <sub>3</sub> gas |                  | = | SO <sub>3</sub> liq. | + (103,240 - 93,680) = 9,560 cal. |

98 lb. of  $\text{H}_2\text{SO}_4$  diluted to 99.5 per cent. strength = 267 C.H.U.  
For 91.4 per cent. acid—

$$n = \frac{8.6 \times 98}{91.4 \times 18} = 0.512$$

then in the same way—

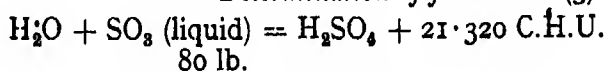
98 lb.  $\text{H}_2\text{SO}_4$  diluted to 91.4 per cent. strength = 3,960 C.H.U.\*

The difference (3,960 - 267), i.e., 3,693 C.H.U., is the heat given out when 99.5 per cent. acid containing 98 parts  $\text{H}_2\text{SO}_4$  is diluted to 91.4 per cent. acid.

Now, 2,056 lb. 91.4 acid = 1,879 lb. of 99.5 per cent. acid + 177 of  $\text{H}_2\text{O}$ .

$$\therefore \text{Heat absorbed} = \frac{3,693 \times 1,879}{98} = 70,800 \text{ C.H.U.}$$

*Determination of factor No. (3).*



$$\therefore 722 \text{ lb.} = \frac{21,320 \times 722}{80} = 192,230 \text{ C.H.U.}$$

*Determination of factor No. (4).*

98 parts monohydrate diluted to 99.5 per cent. acid = 267 C.H.U.

$$\therefore \text{for } \frac{722 \times 98}{80} \text{ lb. } \text{H}_2\text{SO}_4 = \frac{267 \times 722}{80} = 2,410 \text{ C.H.U.}$$

*Determination of factor No. (5).*

Gases are cooled through 20° C.

Disregarding contraction and alterations of density due to formation of  $\text{SO}_3$ , &c., and counting gases as air:—

(1 lb. S gives 10.93 cubic feet  $\text{SO}_2$  at 97.5 per cent. yield.)

$$\text{Heat given up} = \frac{20 \times 0.24 \times 0.08 \times 709 \times 10.93 \times 100}{5} \text{ C.H.U.}$$

$$= 59,520 \text{ C.H.U.}$$

\* This figure is arrived at more easily by using the graph on page 122, Figs. 41 and 42. Thus—

$$100 \text{ lb. of } 99.5 \text{ per cent.} = 99.5 \text{ lb. } \text{H}_2\text{SO}_4 + 0.5 \text{ lb. } \text{H}_2\text{O}$$

$$100 \text{ lb. of } 91.4 = 91.4 \text{ lb. } \text{H}_2\text{SO}_4 + 8.6 \text{ lb. } \text{H}_2\text{O}$$

$$\frac{8.6 \times 99.5}{91.4} =$$

9.36 lb.  $\text{H}_2\text{O}$  required to form 91.4 acid.

but 0.50 lb. already along with 99.5 lb.  $\text{H}_2\text{SO}_4$

$$\therefore \frac{8.86}{100.00} \text{ lb. to be added to } 99.5 \text{ per cent. acid.}$$

giving 108.86 lb. 91.4 per cent. acid.

From the graph, the amount of heat evolved when 100 lb. of 99.5 per cent. of acid is diluted to 91.4 per cent. by addition of 8.86 lb.  $\text{H}_2\text{O}$  is

$$3,750 \text{ C.H.U.}$$

$$\frac{2056 \times 3750}{108.86} = 70,800 \text{ C.H.U. for } 2056 \text{ lb. } 91.4 \text{ per cent. acid.}$$

$$\text{Total} = (1) + (3) + (4) + (5) - (2)$$

$$= 269,690 \text{ C.H.U. per hour generated in System A.}$$

System "B," i.e., front towers and circulating tank.

- (1) Heat of condensation of  $\text{SO}_3$  gas to  $\text{SO}_3$  liquid.
- (2) Resolution of 99.5 per cent. acid into monohydrate and water.
- (3) Solution of liquid  $\text{SO}_3$  in the water formed to give monohydrate.
- (4) Solution of  $\text{SO}_3$  in monohydrate to give 22 per cent. oleum.
- (5) Heat given up by gases in cooling from  $56^\circ$  to  $54^\circ \text{C}$ .

(1) Condensation of  $\text{SO}_3$  gas to  $\text{SO}_3$  liquid.

$$\text{SO}_3 \text{ gas} = \text{SO}_3 \text{ liquid} + 9,560 \text{ C.H.U.}$$

$$80 \text{ lb.} \quad \quad \quad 1$$

$$\therefore 900 \text{ lb.} = \frac{900}{80} \times 9,560 = 107,600 \text{ C.H.U.}$$

(2) 99.5 per cent. acid containing 98 lb.  $\text{H}_2\text{SO}_4$  split up into  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$ .

Require 267 C.H.U.

$$2,778 \text{ lb. 99.5 per cent. acid} = 2,764 \text{ lb. } \text{H}_2\text{SO}_4 + 14 \text{ of } \text{H}_2\text{O}.$$

$$\therefore \text{Heat absorbed} = -267 + \frac{2,764}{98} = -7,530 \text{ C.H.U.}$$

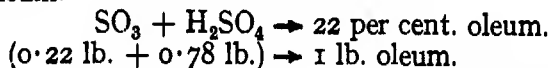
(3) Absorption of Liquid  $\text{SO}_3$  in 14 lb.  $\text{H}_2\text{O}$  to give monohydrate.

$$= \frac{14}{18} \times 21,320 = 16,600 \text{ C.H.U.}$$

(4) Absorption of remaining  $\text{SO}_3$ , i.e.,  $(900 - 62 = 838) \text{ lb.}$  in monohydrate to give 22 per cent. oleum.

This is calculated from the heats of solution in large quantities of water of 22 per cent. oleum, monohydrate, and liquid  $\text{SO}_3$  respectively.

Thus the heat of absorption of liquid  $\text{SO}_3$  in monohydrate = heat of solution of  $\text{H}_2\text{SO}_4$  + heat of solution of  $\text{SO}_3$  liquid - heat of solution of 22 per cent. oleum.



$$(a) \text{ Heat of solution of 1 lb. oleum} = 245 \text{ C.H.U. (Knietseh).}$$

$$(b) \text{ SO}_3 \text{ liq.} + \text{aq.} = 39,180 \text{ ,, (Thomsen).}$$

$$\therefore \text{Heat of solution of 0.22 lb. SO}_3 = 107.7 \text{ ,,}$$

$$(c) \text{ H}_2\text{SO}_4 + \text{aq.} = 17,860 \text{ ,, (Thomsen)}$$

$$\therefore \text{Heat of solution of 0.78 lb. H}_2\text{SO}_4 = 142 \text{ ,,}$$

(b) + (c) - (a) = heat of solution of  $\text{SO}_3$  in monohydrate. That is  $107.7 + 142 - 245 = 4.7 \text{ C.H.U.}$  in the heat of solution of 0.22 lb.  $\text{SO}_3$  in 0.78 lb.  $\text{H}_2\text{SO}_4$ , or—

$$\therefore \frac{4.7}{0.22} = 21 \text{ C.H.U. per 1 lb. of SO}_3 \text{ absorbed.}$$

$$\therefore \text{Heat of absorption of remaining SO}_3 = 838 \times 21 = 17,200 \text{ C.H.U.}$$

(5) Heat given up by converter gases.

$$\frac{2 \times 0.24 \times 0.08 \times 709 \times 10.93 \times 100 \text{ C.H.U.}}{5} = 5,952 \text{ C.H.U.}$$

$$\text{Total :—} = (1) + (3) + (4) + (5) - (2)$$

= 139,820 C.H.U. given out in System B (i.e., in two strong towers and circulating tank).

This heat is dissipated by—

(1) Oleum leaving system—the temperature of this should not exceed 30° C.

(2) Radiation from surface of towers.

(3) Acid coolers.

(1) and (2) are small compared with (3) and may be set off against the decreasing efficiency of the coolers due to gradual sulphating of the interior of the pipes.

#### Coolers.

The oleum cooler has only 280 square feet of surface, so that the duty per square foot per hour is—

$$\frac{139,512}{280} = 500 \text{ C.H.U. per hour per square foot.}$$

The 99 per cent. cooler has 1,220 square feet of surface and the duty is—

$$\frac{269,690}{1,220} = 221 \text{ C.H.U. per hour per square foot.}$$

These calculations refer to 60 lb. charges.

With 90 lb. charges all these figures will be increased by 50 per cent. °

#### Calculation of heat evolved in making 98.5 per cent. acid.

98.5 per cent. acid on 60 lb. charges.

#### Physical data.

S/A	=	91.4 per cent. H <sub>2</sub> SO <sub>4</sub> .
Sulphur burned	=	720 lb. per hour at 98.5 per cent. purity.
		709 lb. pure sulphur.
Per cent. efficiency	=	91.5.
∴ SO <sub>3</sub> produced	=	1,622 lb. per hour.
Temperature of gases to tower 1	=	55° C.
Temperature of exit gases	=	35° C. } Difference = 20° C.

#### Calculation.

$$\begin{array}{lcl} \text{Feed acid per hour} & = & 5,483 \text{ lb.} \\ \text{SO}_3 & = & 1,622 \end{array} \quad \left. \vphantom{\begin{array}{l} 5,483 \\ 1,622 \end{array}} \right\} = \begin{array}{l} 98.5 \text{ per cent. acid formed.} \\ 7,105 \text{ lb.} \end{array}$$

*Thermal system.*

Negative (1) heat of resolution of feed acid into 98.5 per cent. acid and free water.

Positive (2) heat of combination of  $\text{SO}_3$  and free water to form  $\text{H}_2\text{SO}_4$ .

Positive (3) heat of dilution of  $\text{H}_2\text{SO}_4$  (100 per cent.) to 98.5 per cent. acid.

Positive (4) heat of condensation of gaseous to liquid  $\text{SO}_3$ .

(5) heat given up by converter gases.

*Determination of factor (1).*

Affinity of  $\text{H}_2\text{SO}_4$  for  $\text{H}_2\text{O}$  in 98.5 per cent. acid is represented by equation—

$$\text{H}_2\text{SO}_4, n\text{H}_2\text{O} = \frac{n \times 17860}{n + 1.7983}$$

where  $n$  = no. of lb. molecules of water.

98.5 parts  $\text{H}_2\text{SO}_4$  + 1.5 of  $\text{H}_2\text{O}$  = 100 of 98.5 per cent. acid.

i.e., 98 of  $\text{H}_2\text{SO}_4$  require 1.49 of  $\text{H}_2\text{O}$ .

$$\therefore n = \frac{1.49}{18} = 0.0828$$

(a)  $\therefore$  Expression becomes

$$\frac{0.0828 \times 17860}{0.0828 + 1.7983} = 786 \text{ C.H.U. for 98 lb. } \text{H}_2\text{SO}_4.$$

Affinity of 98 parts  $\text{H}_2\text{SO}_4$  contained in acid of 91.4 per cent. strength for the water solute.

91.4 parts  $\text{H}_2\text{SO}_4$  + 8.6 of  $\text{H}_2\text{O}$  = 100 parts of 91.4 per cent. acid.

i.e., 98 of  $\text{H}_2\text{SO}_4$  requires 9.22 of  $\text{H}_2\text{O}$ .

$$n = \frac{9.22}{18} = 0.512$$

$$(b) \quad \therefore \frac{0.512 \times 17860}{0.512 + 1.7983} = 3960$$

$\therefore (b) - (a) = 3960 - 786 = 3,174 \text{ C.H.U. (for 98 lb. } \text{H}_2\text{SO}_4).$

$\text{H}_2\text{SO}_4$  contained in 5,483 lb. feed acid =  $5483 \times 0.914 = 5,011 \text{ lb.}$

$$\therefore (1) = \frac{5011}{98} \times 3174 = 162,300 \text{ C.H.U. (negative).}$$

*Determination of factor (2).*

$\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 21,320 \text{ C.H.U.}$

i.e., 80 lb. liquid  $\text{SO}_3$  give 21,320 C.H.U.

$$\therefore 1,622 \text{ lb.} = \frac{21,320 \times 1623}{80} \text{ C.H.U.} = 432,300 \text{ C.H.U.}$$

*Determination of factor (3).*

80 parts  $\text{SO}_3$  give 98  $\text{H}_2\text{SO}_4$ .

$$\therefore 1,622 \text{ SO}_3 \text{ give } \frac{98 \times 1622}{80} \text{ lb. H}_2\text{SO}_4 \text{ diluted to } 98.5 \text{ per cent}$$

$$\text{acid gives out } \frac{98 \times 1622}{80} \times \frac{786}{98} \text{ C.H.U.} = 15,940 \text{ C.H.U.}$$

*Determination of factor (4).*

$\text{SO}_3$  gaseous =  $\text{SO}_3$  liquid + 9,560 C.H.U.  
80 lb.

$$\therefore 1,622 \text{ lb.} = \frac{9560 \times 1622}{80} = 193,800 \text{ C.H.U.}$$

*Determination of factor (5).**Heat given up by gases.*

Weight of gases: 1 lb. sulphur gives 10.93 cubic feet  $\text{SO}_2$ .  
5 per cent. gas; neglecting contraction, &c., due to formation of  $\text{SO}_3$  and reckoning all gas as air.

$$\text{Mass} = \frac{709 \times 10.93 \times 100}{5} \times 0.08 \text{ lb.}$$

$$\text{sp. ht.} = 0.24$$

$$\text{Fall in temperature} = 20^\circ \text{ C.}$$

$$\therefore \text{C.H.U. given up} = \frac{20 \times 0.24 \times 709 \times 10.93 \times 100 \times 0.08}{5}$$

$$= 59,520 \text{ C.H.U. per hour.}$$

$$\text{Total per hour} = (2) + (3) + (4) + (5) - (1).$$

$$= 432,300 + 15,940 + 193,800 + 59,520 - 162,300.$$

$$\text{Total} = 539,260 \text{ C.H.U. per hour.}$$

This heat is dissipated:—

- (1) By acid cooler (1,220 square feet surface).
- (2) By radiation from absorption towers.
- (3) By raising temperature of acid leaving system.

*Radiation loss.*

This was done by noting the rise in temperature of a suitable liquid contained in a rectangular lead box lagged on all sides except one which was blackened; and was placed parallel to the surface of the tower.

The area of this surface exposed to radiation was 1 square foot.

Practically all radiation takes place in the first four towers, and of these the lower half is hotter than the upper half.

Altogether 50 per cent. of the total surface was taken as radiating, and the value obtained from this was 20,000 C.H.U. per hour, i.e., approximately 4 per cent. of the total heat evolved.

$$\therefore \text{radiation loss} = 20,000 \text{ C.H.U.}$$



*Heat taken away by 98.5 per cent. acid leaving system.*

The temperature of this acid should not exceed  $28^{\circ}\text{C}$ .

Initial temperature of feed acid =  $18^{\circ}\text{C}$ .

Rise in temperature,  $10^{\circ}\text{C}$ .

Heat absorbed by acid leaving = total heat of this acid less heat contained in feed acid.

$$= (7105 \times 0.35 \times 28) - (5483 \times 0.36 \times 18)$$

$$= 69592 - 35,530 = 34,099 \text{ C.H.U.}$$

$$\therefore \text{Heat to be removed by coolers} = 539,260 - (20,000 + 34,099) \\ = 485,160 \text{ C.H.U.}$$

$$\frac{485,160}{1220} = \text{say, } 400 \text{ C.H.U. per square foot per hour for a } 60 \text{ lb. charge.}$$

#### ABSORPTION SYSTEM AT THE GRILLO PLANT, AVONMOUTH, AND COMPARISON OF RESULTS OBTAINED IN THE QUEEN'S FERRY PLANT

**Units for making 98 per cent. acid or 94 per cent. acid.**—On these units 98 per cent. acid is pumped over all six absorption towers, the resulting acid being approximately 99 per cent.

The acid so formed is broken down by water to give 98 per cent., the greater part of which re-circulates, and the remainder either passes out of the system or into the mixing tank to make 94 per cent. acid.

The absorption system is shown diagrammatically below :—

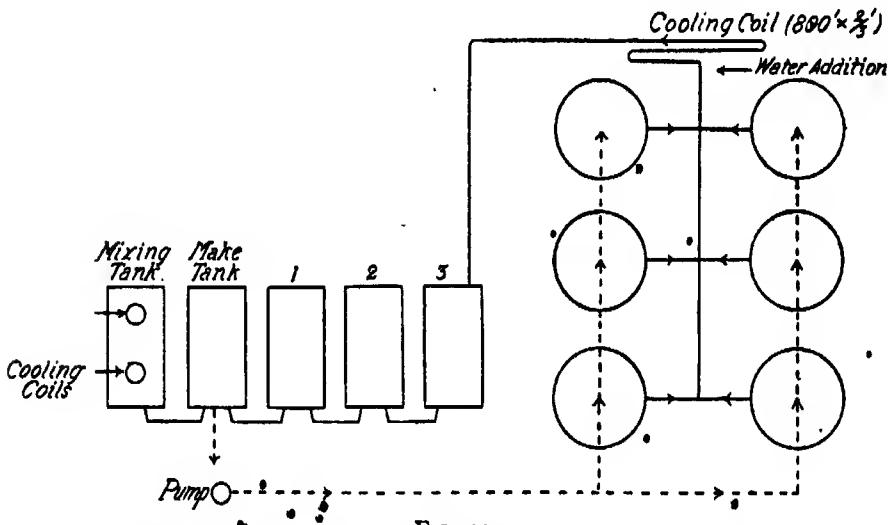


FIG. 33.

**Quantities of  $\text{SO}_3$  and acid involved.**—On a 50 lb. sulphur charge (14 burners, 94 per cent. recovery) the  $\text{SO}_3$  absorbed per hour will be 1,630 lb.

Now, 4.25 lb.  $\text{SO}_3$  added to 100 lb. 98 per cent. acid give 104.25 lb. of 99 per cent. acid.

Therefore, the quantity of 98 per cent. circulating per hour to absorb 1,630 lb.  $\text{SO}_3$  will be 38,350 lb., and the quantity of 99 per cent. so formed will be 39,980.

The 99 per cent. acid will require 420 lb. of water to break it down to 98 per cent. again, of this 38,350 lb. will re-circulate and the remaining 2,050 lb. will either pass out of the system or be broken down in the mixing tank to give 94 per cent. acid.

**Heat-contributing factors.**—The heat to be dissipated in the absorption system from the following factors :—

(1) Heat evolved in adding water to the system, *i.e.*, breaking down the 99 per cent. acid to 98 per cent.

(2) Heat of condensation of gaseous to liquid  $\text{SO}_3$ .

(3) Heat developed by the solution of liquid  $\text{SO}_3$  in 98 per cent. acid to give 99 per cent.

(4) Heat given up by gases passing through the absorption system.

The actual heat effects of these various factors are calculated below.

(1) 100 lb. of 99 per cent. acid plus 1 lb.  $\text{H}_2\text{O}$  giving 101 lb. of 98 per cent.  $\text{H}_2\text{SO}_4$  evolve 500 C.H.U. (from graphs).

Or  $\frac{500 \times 100}{99} = 505$  C.H.U. per 100 lb. of  $\text{H}_2\text{SO}_4$  in form of 99 per cent. acid.

Conversely the amount of heat absorbed in resolving 100 lb. of  $\text{H}_2\text{SO}_4$  in the form of 98 per cent. acid into 99 per cent. acid and free water is — 505 C.H.U.

Therefore, 39,980 lb. of 99 per cent. breaking down to 98 per cent. will evolve—

$$\frac{39,980 \times 500}{100} = 200,000 \text{ C.H.U.}$$

(2)  $\text{SO}_3$  gaseous =  $\text{SO}_3$  liquid + 9,560 C.H.U.

Therefore, 1,630 lb.  $\text{SO}_3 = \frac{9,560 \times 1,630}{80} = 195,000$  C.H.U.

(3) This can be treated as three separate operations—

(a) Resolution of 38,350 lb. of 98 per cent. acid ( $37,600 \text{ H}_2\text{SO}_4$  into 99 per cent. and water  $37,600 \times 505 = - 189,800$  C.H.U.

(b) Absorption of 1,630 lb.  $\text{SO}_3$  in part of this resolved water to form monohydrate—

$\text{SO}_3 \text{ liq.} + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 21,320$  C.H.U.

$$\frac{1,630 \times 21,320}{80} = 434,000$$

(c) Heat of dilution of  $\frac{98 \times 1,630}{80} = 1,996$  lb.

100 per cent.  $\text{H}_2\text{SO}_4$  to 99 per cent. (from graph) approximately + 10,000.

$\therefore$  Total heat for solution of 1,630 lb.  $\text{SO}_3$  in 98 per cent. acid

$$= b + c - a \\ = 254,200 \text{ C.H.U.} \quad \cdot \cdot \cdot$$

(4) The weight of gases passing through the system based on 5 per cent.  $\text{SO}_3$  at converters will be—

1 lb. S = 2 lb.  $\text{SO}_2$ , at 94 per cent. yield =  $2 \times .94 = 1.88$  lb.  $\text{SO}_2$ .

1 lb.  $\text{SO}_2$  = 5.61 cubic feet  $\therefore 1.88 \times 5.61 = 10.55$  cubic feet  $\text{SO}_2$ .

Combustion gas contains 5 per cent.  $\text{SO}_2$ .

$$\therefore \frac{10.55 \times 95}{5} = 200.45 \text{ cubic feet air along with } \text{SO}_2.$$

1 cubic foot air = 0.08 lb —

					Lb.
Air,	$200.45 \times 0.08$	-	-	-	16.04
, $\text{SO}_2$ ,	10.55	-	-	-	1.88

$$\text{Weight of air and } \text{SO}_2 \text{ from 1 lb. S} = \underline{17.92}$$

$50 \times 14 \times 17.92 = 12,544$  lb. = total weight of gas passing through system.

Taking specific heat of gases as 0.23.

Taking fall in temperature as  $20^\circ \text{C}$ .

then  $12,544 \times 0.23 \times 20 = 57,700$  C.H.U.

Thus the total heat generated in the absorption system is 200,000 + 195,000 + 254,200 + 57,700 = 706,900 C.H.U. per hour per 50 lb. S charge.

**Dissipation of heat generated in absorption system.**—A portion of this heat will be lost by radiation from the towers and acid pipes. Experiments at Queen's Ferry have shown this loss to be approximately 5 per cent., say, 35,300 C.H.U. in this case.

Acid leaving the system at  $30^\circ \text{C}$ . (2,050 lb.) and water entering at  $15^\circ \text{C}$ . (400 lb.) while theoretically helping to dissipate the heat of the system are so small in quantity as to be negligible; so that the rest of the heat ( $706,900 - 35,300 = 671,600$  C.H.U.) must be taken out by the acid coolers.

**Work thrown on acid coolers.**—The surface area of the cooling coil =  $800 \text{ feet} \times \frac{2}{3} \text{ feet} \times \pi = 1,675$  square feet.

Therefore, heat to be removed per square foot per hour

$$= \frac{671,600}{1,675} = 400 \text{ C.H.U.}$$

This is for a 50 lb. charge, approximately equal to a 60-lb. For a sulphur charge  $x$ , the work thrown on the cooler would be  $\frac{(400 \times x)}{50}$ .

*Making 94 per cent. acid.*—On a 50 lb. charge the amount of 98 per cent. to be broken down would be 2,050 lb.

100 lb. of 98 per cent. acid plus 4 lb.  $H_2O$  giving 104 lb. of 94 per cent.  $H_2SO_4$  evolve 1,700 C.H.U. (from graph).

Therefore, 2,050 lb. of 98 per cent. will generate  $\frac{2,050 \times 1,700}{100}$  C.H.U.

In the mixing tank there are eight cooling coils, 136 feet long,  $1\frac{1}{2}$  inches diameter, so that surface area =  $136 \text{ feet} \times 8 \times \frac{3}{24} \times \pi$   
= 147 square feet.

The cooler will therefore have to remove—

$$\frac{2,050 \times 1,700}{100 \times 427} = 82 \text{ C.H.U. per square feet per hour on 50 lb. charges.}$$

*Oleum unit.*—In the oleum unit, the first pair of towers make oleum (105 per cent.) and over the four back towers 98 per cent. is circulated, becoming 99 per cent. in so doing. Water is added to the 99–98 per cent. cooler to break down the 99 per cent. acid to 98 per cent. The absorption system is shown diagrammatically below:—

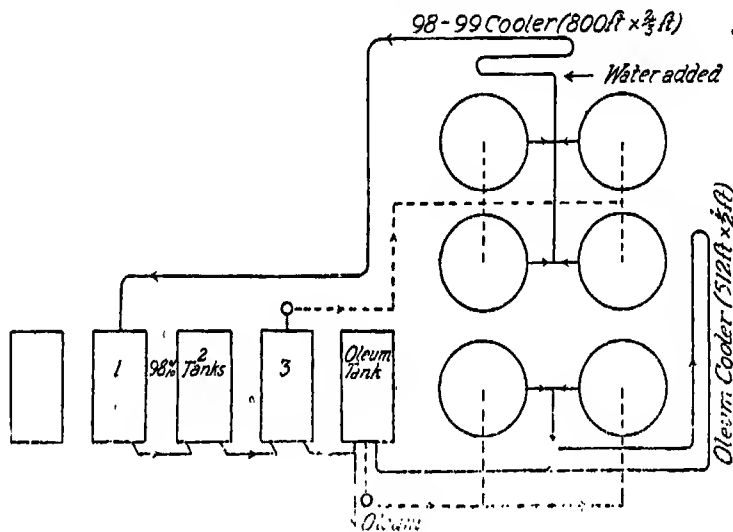


FIG. 34.

*Quantities of acid and  $SO_3$  involved.*—Assuming a 50 lb. sulphur charge, the  $SO_3$  absorbed per hour will be 1,630 lb.

100 lb. 105 per cent. acid = 85.7 lb.  $SO_3$  + 14.3 lb. water.

$\therefore$  amount of water to be added per hour =  $\frac{1,630 \times 14.3}{85.7} = 272 \text{ lb.}$

100 lb. 99 per cent. acid = 80.8 lb.  $SO_3$  + 19.2 lb.  $H_2O$ .

Therefore, amount of  $SO_3$  absorbed in back four towers

$$= \frac{80.8 \times 272}{19.2} = 1,144 \text{ lb.}$$

leaving  $1,630 - 1,144 = 486$  for the oleum towers.

The amount of 99 per cent. acid moving forward to front pair of towers will be  $1,144 + 272 = 1,416$  lb.

*Heat contributing factors in the oleum towers.*—The heat developed will depend on :—

- (1) Condensation of gaseous to liquid  $\text{SO}_3$ .
- (2) Solution of liquid  $\text{SO}_3$  to give oleum.
- (3) Heat given up by gases passing through the towers.

This will be very small. At Queen's Ferry the fall in temperature of the gases is only about  $2^\circ \text{C}$ ., so that this heat effect can be ignored.

Factors (1) and (2) are calculated below.

(1)  $\text{SO}_3$  gas =  $\text{SO}_3$  liquid + 9,560 C.H.U.

$$\therefore 486 \text{ lb. } \text{SO}_3 = \frac{486 \times 9,560}{80} = 58,100 \text{ C.H.U.}$$

(2) This may be taken as three operations—

(a) Resolution of 1,416 lb. 99 per cent. acid into water and monohydrate. The heat effect will be negative and equal in quantity to when water is added to monohydrate to give 99 per cent. acid.

From the graph this works out at 7,000 C.H.U.

(b) Solution of liquid  $\text{SO}_3$  in the resolved water to give  $\text{H}_2\text{SO}_4$ .

$\text{H}_2\text{O} + \text{SO}_3$  (liquid) = 21,320.  
1,416 lb. 99 per cent. acid contains 14 lb.  $\text{H}_2\text{O}$ .

$$\therefore \text{heat effect} = \frac{14}{18} \times 21,320 = 16,400 \text{ C.H.U.}$$

$$\frac{14 \times 80}{18} = 62 \text{ lb. } \text{SO}_3 \text{ hydrated by 99 per cent. acid.}$$

(c) Solution of  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$  to give 105 per cent. oleum.

$\text{SO}_3$  to be absorbed =  $486 - 62 = 424$  lb.

1 lb.  $\text{SO}_3$  absorbed in  $\text{H}_2\text{SO}_4$  to give oleum gives 21 C.H.U.

$$\therefore 424 \text{ lb. } \text{SO}_3 \text{ absorbed in } \text{H}_2\text{SO}_4 \text{ to give oleum gives } 8,900 \text{ C.H.U.}$$

The sum of — (a) + (b) + (c) = 18,300 C.H.U.

The total heat evolved in the oleum absorption towers is therefore—

$$76,400 \text{ C.H.U.}$$

*Dissipation of heat evolved in oleum absorption towers.*—This heat is dissipated by :—

- (1) Oleum leaving the system.
- (2) radiation losses.
- (3) the acid cooler.

The first two factors are small, accounting for about 5 per cent. of the heat, so that approximately 72,000 will have to be removed by the cooler.

*Work thrown on cooler.*—Assuming the cooler to be 512 feet long, as at Queen's Ferry (= 800 square feet), the work will be:—

$$\frac{72,000}{800} = 90 \text{ C.H.U. per square feet per hour on 50 lb. charges.}$$

*Heat-contributing factors in the 99-98 per cent. system.*—The heat developed here will depend on—

(1) The water added to the cooler to break down the 99 per cent. acid to 98 per cent.

(2) The condensation of gaseous to liquid  $\text{SO}_3$ .

(3) The solution of liquid  $\text{SO}_3$  in 98 per cent. acid to give 99 per cent.

(4) The heat given up by the gases passing through the absorption towers.

(1) The amount of  $\text{SO}_3$  absorbed = 1,144 lb.

98 per cent. acid =  $80 \text{ SO}_3 + 20 \text{ H}_2\text{O}$ .

99 per cent. acid =  $80.82 \text{ SO}_3 + 19.18 \text{ H}_2\text{O}$ ; or

$$\frac{80.82 \times 20}{19.18} = 84.25 \text{ SO}_3 + 20 \text{ H}_2\text{O}.$$

$\therefore$  to 100 lb. 98 per cent. acid must be added

$$84.25 - 80 = 4.25 \text{ SO}_3$$

in order to form 104.25 lb. 99 per cent. acid.

$$\therefore \frac{104.25 \times 1,144}{4.25} = 28,000 \text{ lb. 99 per cent. acid will be formed.}$$

The heat evolved on breaking down 99 per cent. to 98 per cent. is 500 C.H.U. for 100 lb. 99 per cent. acid (from the graph), or 505 C.H.U. for 100 lb.  $\text{H}_2\text{SO}_4$  as 99 per cent.

$$\therefore \frac{28,000 \times 500}{100} = 140,000 \text{ C.H.U.}$$

(2)  $\text{SO}_3$  (gas) =  $\text{SO}_3$  (liquid) + 9,560 C.H.U.

$$9,560 \times 1,144 = 136,700 \text{ C.H.U. for 1,144 lb. SO}_3$$

(3) This may be taken as three operations:—

(a) Resolving 98 per cent.  $\text{H}_2\text{SO}_4$  into 99 per cent. and water.

(b) Dissolving the  $\text{SO}_3$  in the resolved water to give  $\text{H}_2\text{SO}_4$ .

(c) Breaking down the  $\text{H}_2\text{SO}_4$  to 99 per cent. sulphuric acid.

(a) This is negative and = - 505 C.H.U. for each 100 lb.  $\text{H}_2\text{SO}_4$  as 98 per cent. acid, i.e.—

$$28,000 - 1,144 = 26,856 \text{ lb. 98 per cent. acid.}$$

$$= 26,300 \text{ lb. 100 per cent. H}_2\text{SO}_4.$$

$$\therefore 26,300 \times - 505 = - 133,000 \text{ C.H.U.}$$

(b)  $\text{H}_2\text{O} + \text{SO}_3$  (liquid) = 21,320 C.H.U.

$$\frac{21,320 \times 272}{18} = 322,600 \text{ C.H.U. for 272 lb. H}_2\text{O}.$$

(c) Calculating from the graph this is 7,600 C.H.U.

$$- a + b + c = 196,600 \text{ C.H.U.}$$



Nº 1.

# OLEUM UNIT.

## HEAT GENERATED IN OLEUM SYSTEM.

(2 TOWERS)

AT  
AVONMOUTH

AT  
QUEEN'S FERRY

SO <sub>3</sub> Gas to SO <sub>3</sub> liquid
58,100 C.H.U.
Solution SO <sub>3</sub> 18,300

SO <sub>3</sub> gas to SO <sub>3</sub> liquid
107,600 C.H.U.
Solution SO <sub>3</sub> 26,500
From gases 5,900

Work thrown on Steel Coolers, C. H. U. per Sq. ft. per Hour  
Cooler = 512 ft<sup>2</sup> x 6-in = 800 Sq. ft. Avonmouth  
Cooler = 280 Sq. ft. Queen's Ferry.

Avonmouth  
90

Queen's Ferry 500

## HEAT GENERATED IN 98% SYSTEM.

(4 TOWERS)

AT  
AVONMOUTH

WORK THROWN  
ON  
COOLERS  
AT

Adding Water Feed
144,000 C.H.U.
SO <sub>3</sub> gas to SO <sub>3</sub> liquid
137,000 C. H. U.
Solution of SO <sub>3</sub> liquid
192,500 C.H.U.
From gases
57,700

QUEEN'S FERRY

AVONMOUTH

QUEEN'S FERRY

Adding 90% Feed
SO <sub>3</sub> gas to SO <sub>3</sub> liquid
86,280
Solution of SO <sub>3</sub> liquid
123,800
From gases
59,500

300 C. H. U.

220 C. H. U.

Cooler = 1675 Sq. ft. Avonmouth  
Cooler = 1220 Sq. ft. Queen's Ferry

FIG. 35.





Nº 2

98% ACID UNIT.

HEAT GENERATED IN  
ABSORPTION SYSTEM  
AT  
AVONMOUTH

Adding Water Feed 200,000 C.H.U.
SO <sub>2</sub> gas to SO <sub>2</sub> liquid 195,000 C.H.U.
Solution of SO <sub>2</sub> liquid 254,200
Heat from Gases 57,700

HEAT GENERATED IN  
ABSORPTION SYSTEM  
AT  
QUEEN'S FERRY

Adding 90% Feed
SO <sub>2</sub> gas to SO <sub>2</sub> liquid 194,000 C.H.U.
Solution of SO <sub>2</sub> liquid 286,000
Heat from Gases 59,500

Work Thrown on Cast-iron Coolers.  
per Sq Foot per Hour in C.H.U.

Cooler = 1675 Sq. Ft. Avonmouth.

Cooler = 1220 Sq. Ft. Queen's Ferry.

Avonmouth 410

Queen's Ferry 440

FIG. 36.

(4) Assuming fall in temperature of gases is  $20^{\circ}$  C., then the heat given out will be the same as in 99-98 unit, viz.,

$$57,700 \text{ C.H.U.}$$

The total heat generated in the system will therefore be

$$140,000 + 133,000 + 170,000 + 57,700 = 520,700 \text{ C.H.U.}$$

*Dissipation of heat generated in the system.*—A portion of this heat will be dissipated by radiation (say, 5 per cent.), leaving the remainder, 500,300, to be taken by the acid cooler.

The surface area of the cooler (as in 98 per cent. unit)

$$= 1675 \text{ square feet.}$$

$\therefore$  work thrown on cooler is

$$\frac{500,300}{1675} = 300 \text{ C.H.U. per square foot per hour per 50 lb. charge.}$$

*Comparisons between Queen's Ferry and Avonmouth plants.*—The heat effect in the Queen's Ferry absorption system, where, approximately, 90 per cent. acid is used as feed instead of water, has been previously calculated.

The figures there were based on a 60 lb. charge, which is, approximately, equal to Avonmouth 50 lb. charge. The results of the comparison, both of the heat evolved and the work thrown on the coolers, are shown in graphical form on Figs. 35 and 36.

From these it will be seen that:—

(1) The extra heat developed at Avonmouth due to water feed is counterbalanced by the extra length of cooler, so that in the 98 per cent. (or 94 per cent.) unit, approximately, the same work is thrown on the cooler (400 C.H.U.).

(2) In making oleum at Avonmouth a greater proportion of heat is developed in the 98 per cent. system than at Queen's Ferry.

This and the heat due to water feed causes a difference in the work thrown on the coolers; giving 90 C.H.U. to the oleum and 300 C.H.U. to the 98 per cent. cooler.

#### PLANT FOR BREAKING DOWN OLEUM OR STRONG SULPHURIC ACID BY MEANS OF WATER

It is often necessary to dilute oleum or strong sulphuric acid with water.

Owing to the large amount of heat evolved and violence of the reaction, special precautions have to be taken to remove the heat and prevent undue corrosion of the plant.

The following arrangement is the result of many trials and worked well:—

Oleum is fed from the storage tank into a feed box, 10 inches  $\times$  14 inches  $\times$  15 inches deep, made of cast-iron and divided diagonally

into two compartments by a cast-iron  $\frac{1}{2}$  inch plate, punched diagonally with  $\frac{7}{16}$  inch holes. This ensures a constant quantity being fed into the plant; each hole corresponds to a given amount of oleum. From the feed box the oleum is fed by a  $1\frac{1}{2}$  inch cast-iron pipe through a cast-iron *sight box*, as a further aid to constant feed, and then by a  $1\frac{1}{2}$  inch cast-iron pipe into the *mixing pot* (Fig. 37).

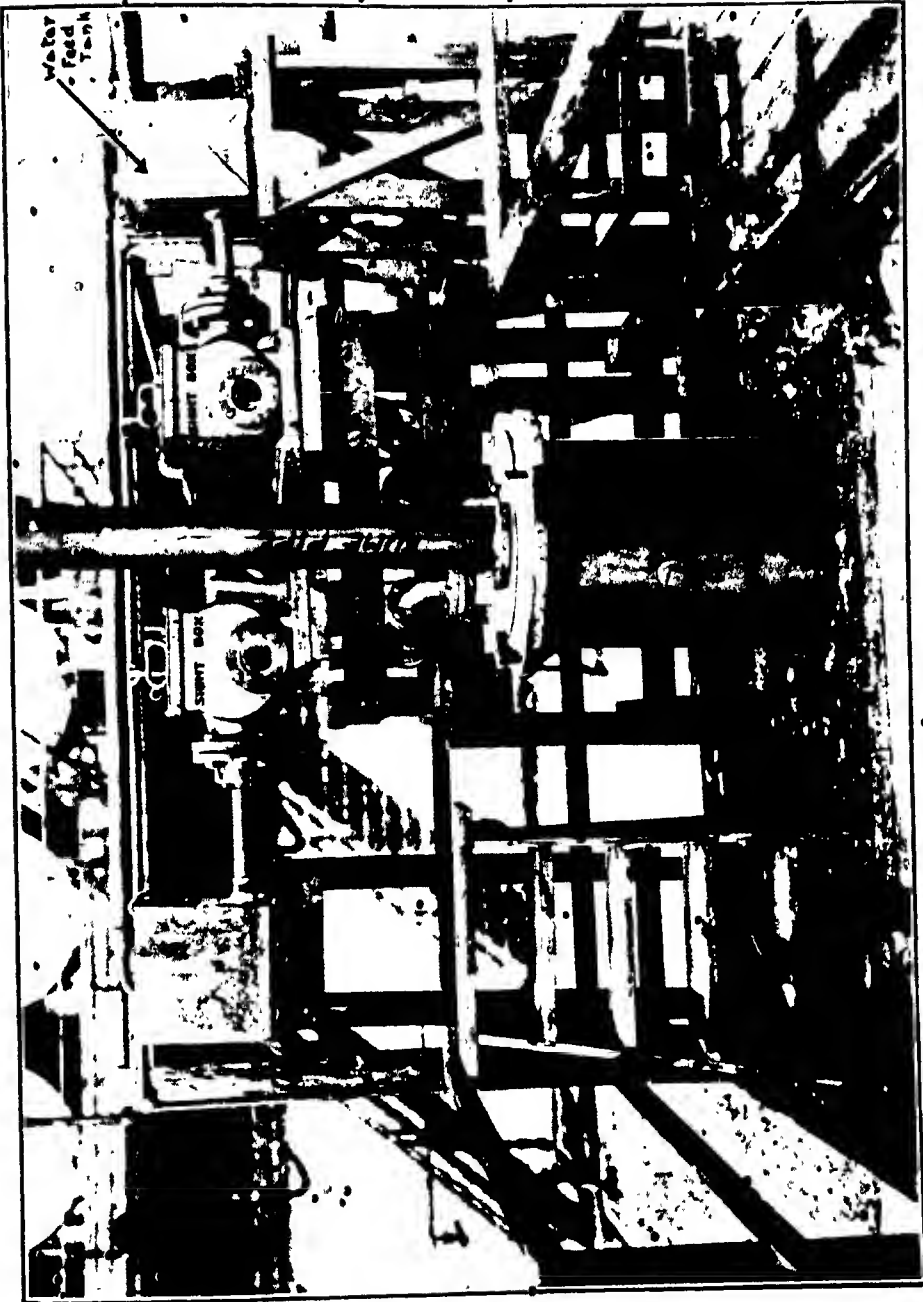
This was a cast-iron pipe, 18 inches internal diameter, 4 feet long. It is blank flanged at both ends and stands vertical. The top blank was bored to take the  $1\frac{1}{4}$  inch inlet pipes for oleum and water, and also to allow a 5 inch cast-iron pipe, 8 feet long, to be erected as a miniature fume main for the pot. The bottom blank flange was tapped to take a  $2\frac{1}{2}$  inch cast-iron pipe as an outlet for the acid. The whole of the inside of the pot was lined with a thin layer of "obsidianite" acid-proof brick, using volvic and asbestos powder (equal parts) and silicate of soda and water (4 to 1) as a jointing material. Water is fed to the mixing pot just in the same way as the oleum is fed, with the exception that the feed box in this case is of lead, but otherwise identical with that described above. The outlet for the acid rises on leaving the bottom of the pot, so that the mixing pot is always kept half full of acid. The outlet pipe then descends and enters the cooler. At the point where the outlet pipe ceases to ascend and commences to descend into a cooler, a  $\frac{1}{2}$  inch cast-iron pipe, 2 feet high, is tapped into the pipe to act as a "vent-pipe" to avoid air blocks. Both the water and oleum feeds to the mixing pot finish underneath the constant level of the acid in the pot. These feeds leave the sight boxes as  $1\frac{1}{2}$  inch cast-iron pipes, but change on entering the mixing pot, to earthenware. Thus, by using earthenware pipes and acid-proof lining, corrosion is reduced to a minimum.

#### THE COOLERS (Figs. 38, 39, 40)

The coolers consist essentially of 48, 9 foot lengths of 6 inch cast-iron tubing, arranged in four columns, each column containing six 18 foot (two 9 foot lengths) lengths one above the other. The cooler is thus 432 feet long apart from the bends. It is arranged in two halves joined by a  $2\frac{1}{2}$  inch cast-iron pipe fitted with a T piece and valve, so that if at any time one of the lengths require renewal, a hand pump can be attached to the valve and the cooler drained of acid. The acid flows down one half through the  $2\frac{1}{4}$  inch connecting pipe and up the other half, finally being discharged through a  $2\frac{1}{2}$  inch outlet pipe into a stock tank. This discharge pipe is higher than the cooler, in order to keep the latter continually full of acid to prevent corrosion. The stock tank is a circular mild steel reservoir as used in the Mannheim plant. From this tank a  $1\frac{1}{4}$  inch centrifugal pump lifts the product, 94 per cent. acid, to the storage tank.

The water is sprayed on to the top of the four columns of piping. Thus, in the first half, we have the hottest acid meeting the coolest water. Unscientific as this may seem, it could not be avoided owing to the difficulty of head required to keep the cooler full and still keep the flow sufficient to meet demands. In the second half of the cooler the

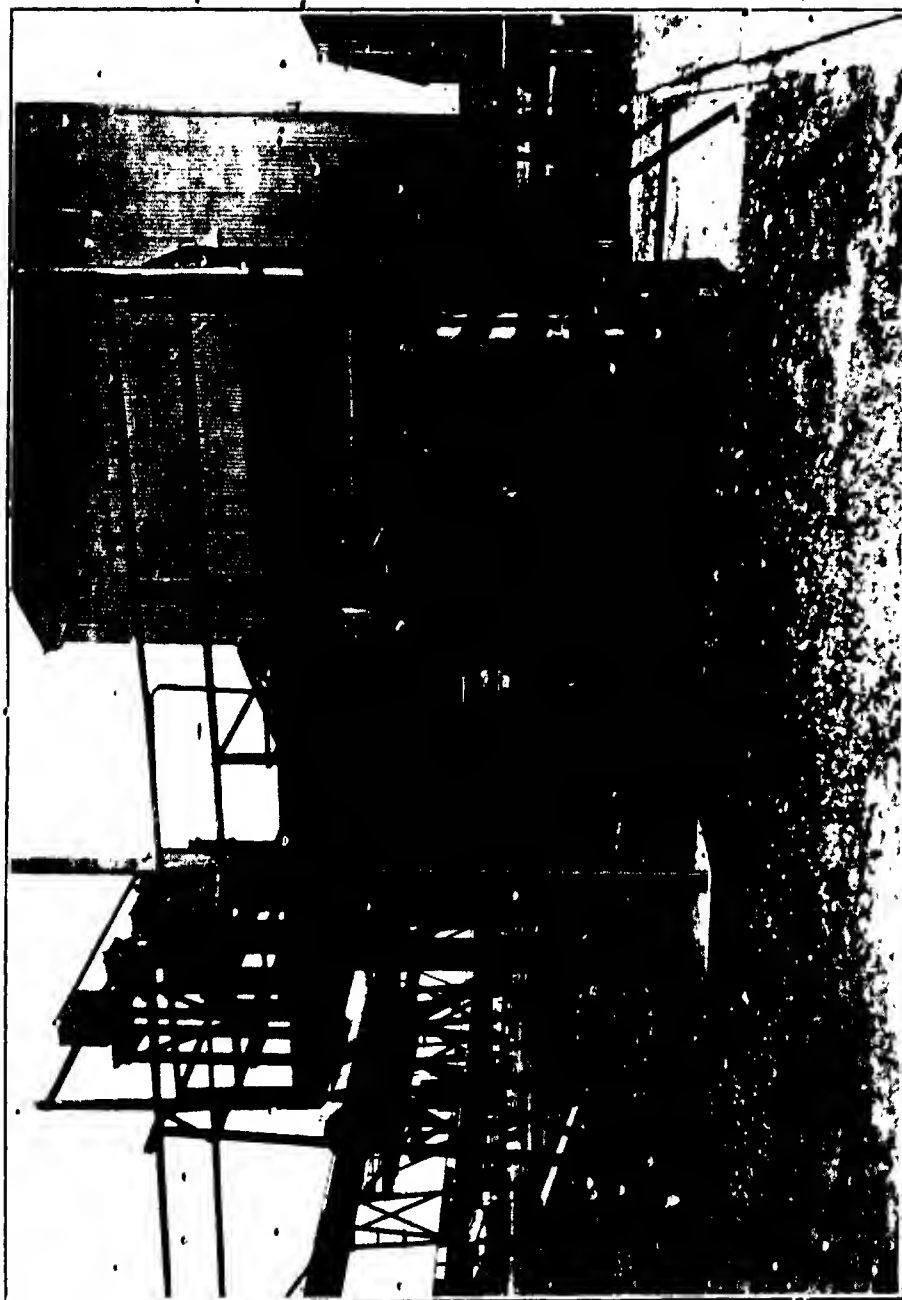
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is therefore of a much higher standard.

The whole of the piping is of standard lengths, which makes the question of renewals an easy one to face.

Pitchpine boards are placed vertically between the pipes to aid water distribution.

The plant stands on a base of acid-proof brick with sulphur jointings. This floor is edged on three sides with two courses of acid-proof brick, and has a 10 inch fall to the drain which flows along the fourth side.

The plant will break down sufficient oleum to provide feed acid for all four units on a 90 lb. charge.

The plant was designed upon the following calculations:—Burning 90 lb. sulphur per burner per hour and assuming a 90 per cent. conversion, the feed acid of 94 per cent. required to absorb the  $\text{SO}_3$  produced per unit of 12 burners per hour is 1.79 tons. For four Grillo units this will be 7.16 tons per hour. The heat rise when oleum is mixed with water to give 94 per cent. acid is taken as  $150^\circ \text{C}$ . A 6 inch cast-iron pipe of the type in use when water cooled will give up to the water 1,000 C.H.U. per square foot per hour. Calculations are made to give the resulting acid at  $25^\circ \text{C}$ . A 6 inch iron pipe has a circumference of 19 inches, i.e.  $\frac{19}{12}$  feet.

C.H.U. per hour produced = sp. heat of 94 per cent. acid  $\times$  lb. 94 per cent. acid  $\times$  temperature differential

$$= .37 \times (7.16 \times 2240) \times (150 - 25) = 742000.$$

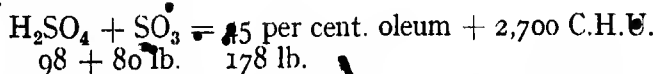
$$\text{Number square feet cooling surface required} = \frac{.37 \times 7.16 \times 2240 \times 125}{1000}$$

$$\text{Number of feet run of pipe required} = \frac{.37 \times 7.16 \times 2240 \times 125 \times 12}{1000 \times 19} = 468 \text{ feet.}$$

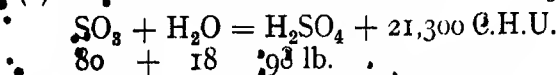
#### HEAT EVOLVED IN BREAKING DOWN OLEUM

We have to consider—

(1) Heat absorbed in resolution of 20 per cent. oleum into  $\text{H}_2\text{SO}_4$  and  $\text{SO}_3$ .



(2) Heat evolved in conversion of free  $\text{SO}_3$  to  $\text{H}_2\text{SO}_4$ .



(3) Heat evolved in dilution of  $\text{H}_2\text{SO}_4$  (100 per cent.) to sulphuric acid 94 per cent.

(1) This factor is small compared with (2) and (3).

20 per cent. oleum = 98 lb.  $\text{H}_2\text{SO}_4$  + 24.5 lb.  $\text{SO}_3$

45 per cent. oleum = 98 lb.  $\text{H}_2\text{SO}_4$  + 80 lb.  $\text{SO}_3$  + 2,700 C.H.U.

$\therefore x$  may be taken as approx.  $\frac{2700}{3.26} = 830$  C.H.U.

(This value is negative.)

(2) 100 lb. 20 per cent. oleum = 80 lb.  $\text{H}_2\text{SO}_4$  + 20 lb.  $\text{SO}_3$ .

100 lb. oleum + 4.5  $\text{H}_2\text{O}$  = 104.5 lb.  $\text{H}_2\text{SO}_4$  + 5,330 C.H.U.

$$\left( \frac{21300 \times 4.5}{18} = 5330 \right)$$

$\therefore$  formation of 98 lb. monohydrate gives

$$\frac{98 \times 5330}{104.5} = 5,000 \text{ C.H.U.}$$

(3)  $(\text{H}_2\text{SO}_4, n \text{ H}_2\text{O}) = \frac{n \times 17860}{n + 1.7983}$  dilution of  $\text{H}_2\text{SO}_4 = H$ , heat of dilution.

98 lb.  $\text{H}_2\text{SO}_4$  + 6.2 lb.  $\text{H}_2\text{O}$  = 104.2 lb. 94 per cent. acid + H.

From equation,  $n = \frac{6.2}{18} = 0.344$ .

$$\text{Then heat of dilution} = \frac{0.344 \times 17860}{0.344 + 1.7983}$$

$$H = 2,870 \text{ C.H.U.}$$

Combining (1), (2) and (3) we get (to produce 104.2 lb. 94 per cent. acid from 20 per cent. oleum and water) :—

122.5 lb. oleum split into  $\text{H}_2\text{SO}_4$  and  $\text{SO}_3$  — 830 C.H.U.

93.78 lb. oleum split into  $\text{H}_2\text{SO}_4$  and  $\text{SO}_3$  — 635 C.H.U.

but 93.78 oleum yield 98 lb. monohydrate.

$\therefore$  In formation of 98 lb. monohydrate from 20 per cent. oleum heat evolved = 5,000 — 635 = 4,365 C.H.U.

Heat evolved in diluting 98 lb. monohydrate to 104.2 lb.

94 per cent. acid = 2,870 C.H.U.

$\therefore$  Total heat evolved in formation of 104.2 lb. 94 per cent. = 4,365

+ 2870 = 7235 or  $\frac{7235}{104.2} = 69.4$  C.H.U. per lb. of 94 per cent. acid formed.

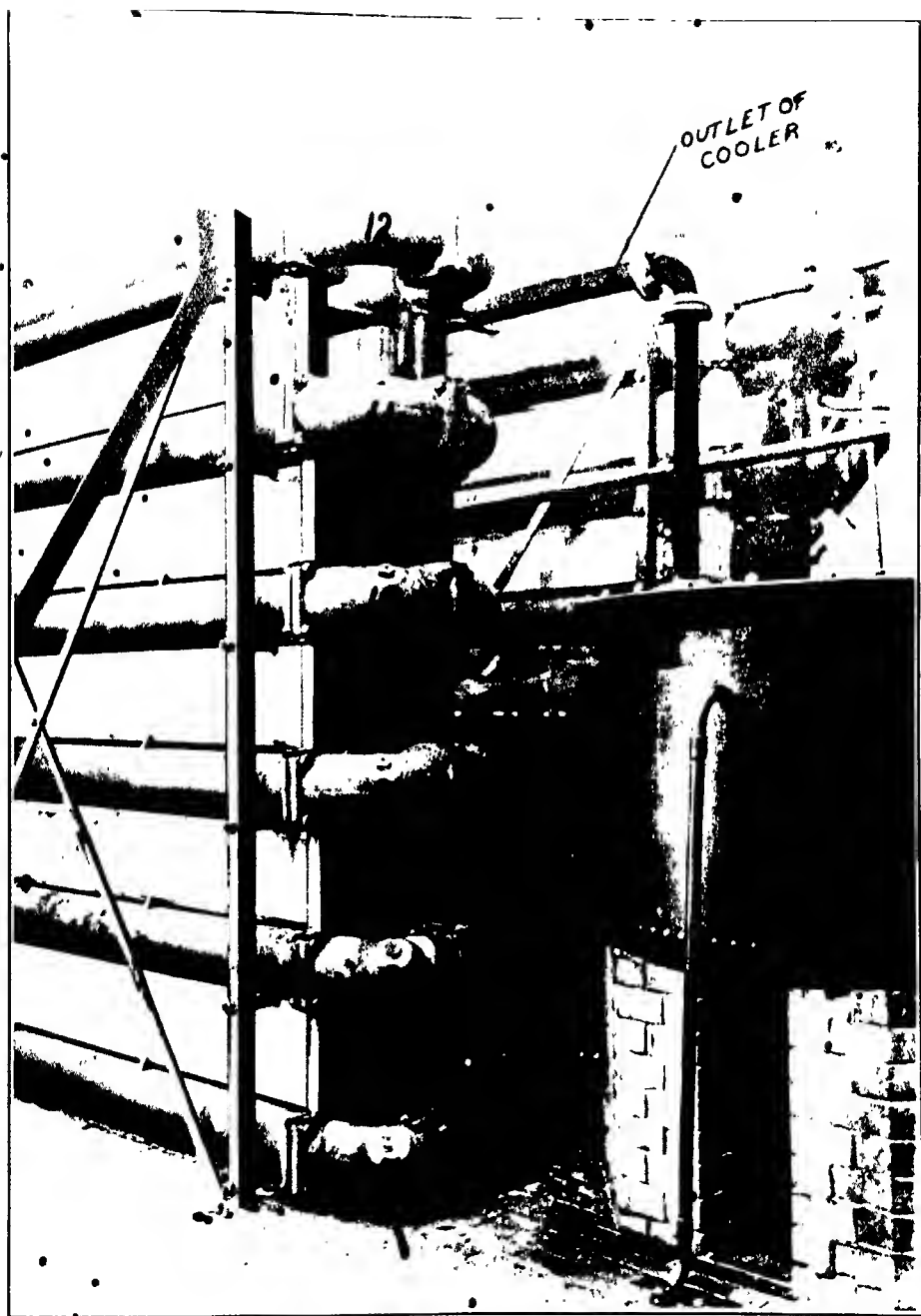
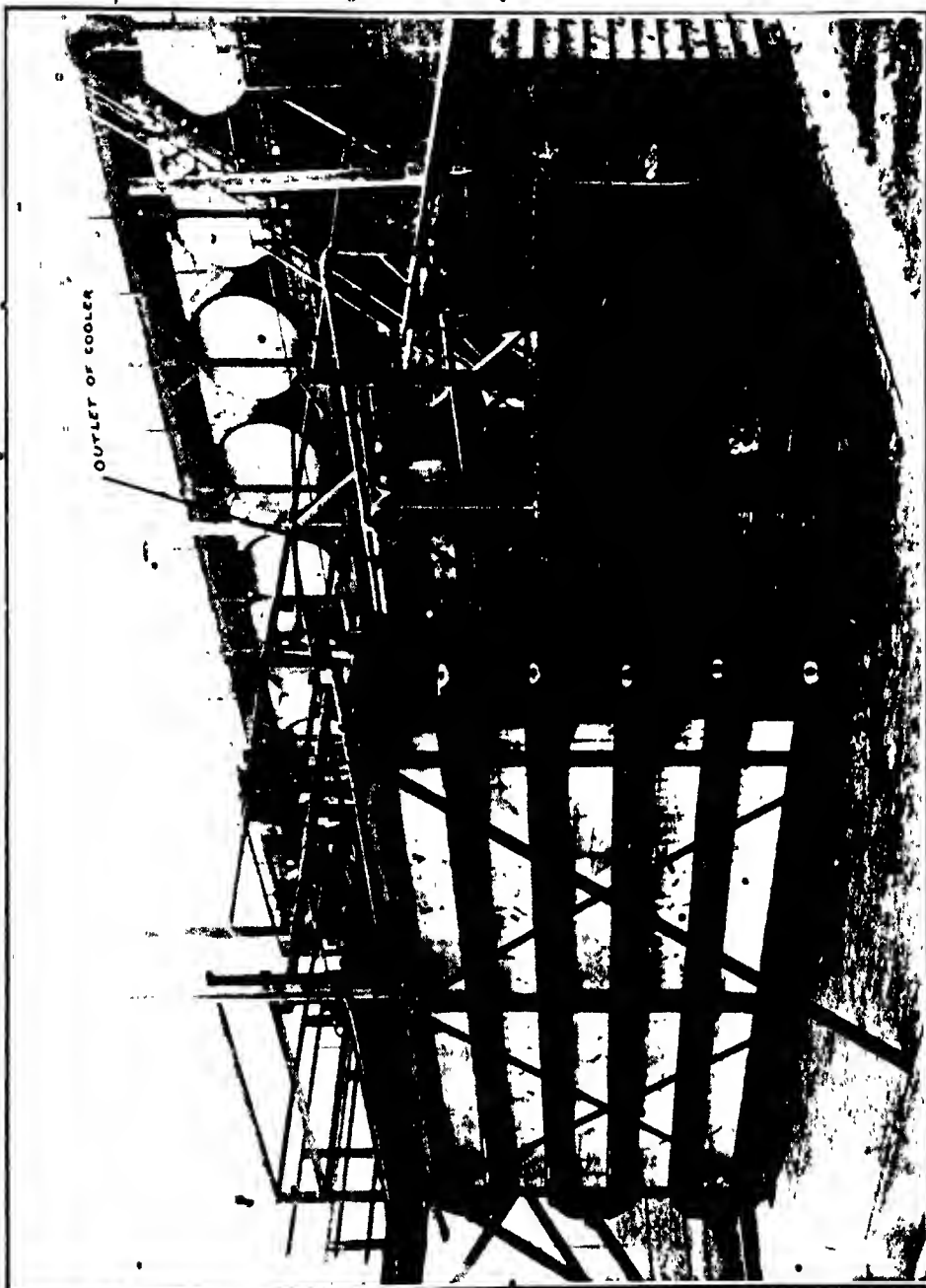


FIG. 39







## APPENDIX I

The following calculations and graph have been found useful in ascertaining the heats of dilution of different strengths of sulphuric acid.

The observed values of the heat of dilution of sulphuric acid agree fairly well with the equation proposed by Julius Thomsen :—

$$(1) \quad H' = \frac{17860 \times x}{x + 1.798}$$

in which  $H'$  is the number of gram calories evolved when  $x$  gram molecules of water are added to one gram molecule of pure sulphuric acid.

For practical purposes it is more convenient to transform the above into an equation giving the Heat  $H''$ , which is evolved when  $y$  gram of water are added to 100 grams of  $H_2SO_4$ . From equation (1)  $H'$  is the heat evolved by the addition of  $18x$  grams of water to 98 grams of  $H_2SO_4$ .

$$\text{Hence} \quad H' = \frac{100}{98} H'' \text{ and } y = \frac{100}{98} \times 18x$$

$$\text{or} \quad x = \frac{98y}{1800}$$

The equation for  $H''$  is therefore—

$$H'' = \frac{100}{98} \times \frac{17860 \times 98y}{1800 + 1.798}$$

$$(2) \quad \text{or} \quad H'' = \frac{1786000y}{98y + 3236} \text{ calories.}$$

A more general case is that in which  $z$  grams of water are added to 100 grams of an acid consisting of  $x$  grams of water to  $(100 - x)$  grams of  $H_2SO_4$ . The heat evolved in this reaction is clearly the difference between the heats evolved when  $(x + z)$  grams and  $x$  grams respectively are added to  $(100 - x)$  grams of  $H_2SO_4$ .

In order to apply equation (2), which may conveniently be written in the form :

$$H'' = \frac{ay}{by + c}$$

it must be noticed that we start with an acid of the composition of

$\frac{100x}{(100-x)}$  grams of water to 100 grams of  $H_2SO_4$ , and finish with acid of

the composition of  $\frac{100(x+z)}{(100-x)}$  grams of water to 100 grams of  $H_2SO_4$ .

Hence if we were dealing with 100 grams of  $H_2SO_4$ , the heat of dilution would be—

$$\frac{\frac{100a(x+z)}{(100-x)}}{\frac{100b(x+z) + c}{(100-x)}} = \frac{\frac{100ax}{(100-x)}}{\frac{100bx + c}{(100-x)}}$$

In reality, however, we are dealing with only  $(100 - x)$  grams of  $H_2SO_4$ , so that the actual heat of dilution,  $H$  is given by the equation—

$$H = \frac{(100 - x)}{100} \left\{ \frac{100a(x + z)}{(100 - x)} + \frac{100ax}{(100 - x)} \right\}$$

$$H = \frac{(100 - x)}{100} \left\{ \frac{100b(x + z) + c}{(100 - x)} + \frac{100bx + c}{(100 - x)} \right\}$$

or 
$$H = \frac{1000z(100 - x)^2}{(100bx + c)(100 - x)(100bx + c)(100 - x) + 100bz}$$

Putting in the values of  $a$ ,  $b$  and  $c$  respectively as given in equation (2) and simplifying we have finally:—

$$(3) \quad H = \frac{1000z(100 - x)^2}{(2.029x + 100)(3.676x + 5.487z + 181.2)}$$

or 
$$H = \frac{1000z(100 - x)^2}{Q(2.029x + 100)}$$

where 
$$Q = (3.676x + 5.487z + 181.2).$$

If the reacting quantities are given in grams,  $H$  will be expressed in gram calories, whilst if the reacting quantities are in lb.,  $H$  will be in lb.-centigrade units (C.H.U.).

**Construction of graphs for solving the general equation for  $H$ .**—The most convenient type of graph for solving this equation is the "alignment chart." Two graphs will be necessary:—

Fig. 41 for solving the equation:

$$Q = (3.676x + 5.487z + 181.2)$$

and second, Fig. 42, with logarithmic scales, for solving the equation:

$$H = \frac{1000z f(x)}{Q}$$

in which 
$$f(x) = \frac{(100 - x)^2}{(2.029x + 100)}.$$

In Fig. 41 the same unit of length, say, a millimetre, may be used on both the  $x$  and  $z$  axes. The  $Q$  axis will, therefore, be midway between the  $x$  and  $z$  axes, and the unit of length will be half the unit on  $x$  or  $z$ . On the  $x$  axis, plot  $x$  as  $3.676x$ , and on the  $z$  axis, plot  $z$  as  $5.487z$ . On the  $Q$  axis, plot as  $(Q - 181.2)$ .

In Fig. 42 the scales are logarithmic. On the  $x$  axis  $x$  is plotted as  $\log f(x)$ . On the several axes the unit of the length chosen, say the millimetre, has the following value in terms of the logarithm:

On the $x$ axis	0.003.
on the $Q$ axis	0.002.
on the $z$ axis	0.006.
On the $H$ axis	0.011.



# HEAT OF DILUTION OF SULPHURIC ACID.

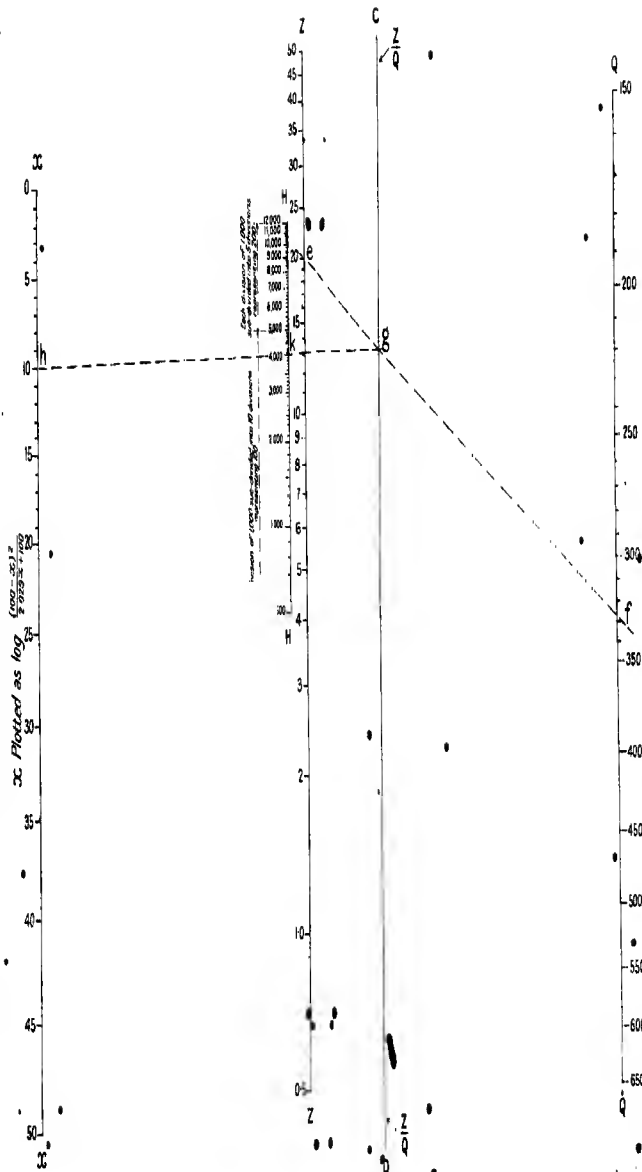
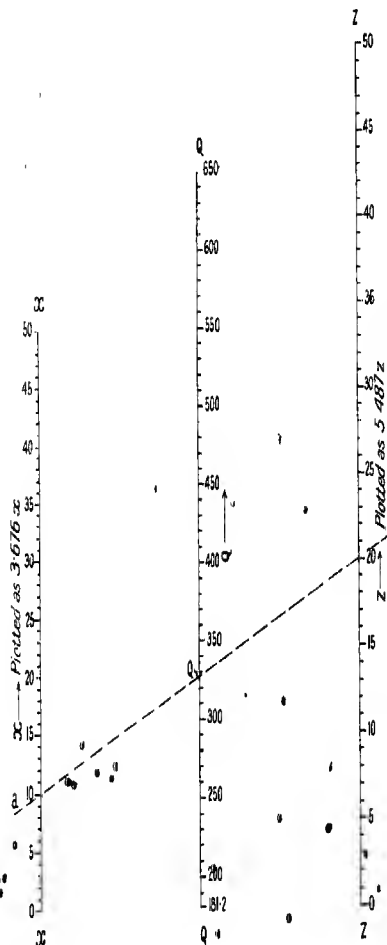
If  $Z$  parts of water are added to an acid containing  $X$  parts of water to  $(100-X)$  parts of  $H_2SO_4$ , the heat evolved is given by equation:-

$$H = \frac{(3.676X + 5.487Z + 181.2)}{100}$$

$H$  will be in gram calories or lb-centigrade units (C.H.U.) according to whether the weights of the substances are in grams or lb. To find  $H$  from the graphs,  $Q$  is first found from FIG. 41. Next lay a straight-edge on the values of  $Q$  &  $Z$  on the axes to the right of FIG. 42, and mark the intersection with the axis C.D. Then join this point with the value of  $X$  on the  $X$ -axis and read off the answer on the  $H$ -axis.

## EXAMPLE:-

20 lb. of water were added to 100 lb. of acid containing 10 lb. of water to 90 lb.  $H_2SO_4$ . Here  $x=10$  and  $z=20$ . In FIG. 41, join 10 on the  $X$ -axis with 20 on the  $Z$ -axis by the line a-b and the intersection of a-b with the  $Q$ -axis gives  $Q=327.7$ . Then in FIG. 42, join 327.7 on the  $Q$ -axis with 20 on the  $Z$ -axis by the line e-f and note the intersection with support C.D. at g. Lastly join g with 10 on the  $X$ -axis (line g-h) and intersection of g-h with the  $H$ -axis at k gives  $H=400$  C.H.U.





The distance of the support  $Cd$  from the  $Q$  and  $z$  axes, respectively, must therefore be as 3 to 1, and the distance of the  $H$  axis from the  $CD$  and the  $x$  axes, respectively, must be as 3 to 8. The actual position of the unit point (zero of the logarithm) on the  $Q$ ,  $z$  or  $x$  axis is immaterial. The position of the unit point on the  $H$  axis is found graphically by solving special examples, the position of the scale of  $H$  being adjusted to agree with the points so found. The following examples may be used:—

$x$	$z$	$Q$	$H$	$\log H - 3$
10	10	272.9	2467	.3932
20	20	364.4	2502	.3983
30	30	456.1	2003	.3017
10	20	327.7	4110	.6138

A transparent straight-edge of glass or celluloid or a stretched thread may be used for reading the graphs.

APPENDIX II

HUMIDITY OF AIR, AND ALLIED DATA

*Partial pressures of water vapour and air.*

*Weight of water per unit volume of air at various temperatures and degrees of humidity.*

*Weight of water required to saturate unit volume of air at various temperatures and initial degrees of humidity.*

*Weight of water per unit weight of air.*

*Heat absorbed by evaporation of water.*

SECTION I.

*Partial pressures of water vapour and air and weight of water per unit volume of air.*

Table I.

*Partial pressure in atmospheres of water vapour in air at various degrees of humidity or percentages of saturation at various temperatures, the total pressure being 1 atm.*

Temp. ° C.	Degree of Humidity or Percentage of Saturation.									
	10 %	20 %	30 %	40 %	50 %	60 %	70 %	80 %	90 %	100 %
0°	·001	·001	·002	·002	·003	·004	·004	·005	·005	·0061
5°	·001	·002	·003	·004	·005	·005	·006	·007	·008	·0085
10°	·001	·002	·004	·005	·006	·007	·008	·010	·011	·0121
15°	·002	·003	·005	·007	·009	·011	·012	·014	·015	·0168
20°	·002	·005	·007	·009	·012	·014	·016	·018	·021	·0230
25°	·003	·006	·009	·012	·016	·019	·022	·025	·028	·0312
30°	·004	·008	·013	·017	·021	·025	·029	·034	·038	·0417
35°	·006	·011	·017	·022	·028	·033	·039	·044	·050	·0553
40°	·007	·015	·022	·029	·037	·044	·051	·058	·065	·0725
45°	·009	·019	·028	·038	·047	·056	·066	·075	·085	·0944
50°	·012	·024	·036	·048	·061	·073	·085	·097	·109	·1214

Table II.

*Partial pressures in atmospheres of the net dry air in moist air of various degrees of humidity or percentages of saturation at various temperatures, the total pressure being 1 atm.*

Temp. ° C.	Degree of Humidity or Percentage of Saturation.									
	10 %	20 %	30 %	40 %	50 %	60 %	70 %	80 %	90 %	100 %
0°	·999	·999	·998	·998	·997	·996	·996	·995	·995	·994
5°	·999	·998	·997	·996	·995	·995	·994	·993	·992	·991
10°	·999	·998	·996	·995	·994	·993	·992	·990	·989	·988
15°	·998	·997	·995	·993	·991	·990	·988	·986	·985	·983
20°	·998	·995	·993	·991	·988	·986	·984	·982	·979	·977
25°	·997	·994	·991	·988	·984	·981	·978	·975	·972	·969
30°	·996	·992	·987	·983	·979	·975	·971	·966	·962	·958
35°	·994	·989	·983	·978	·972	·967	·961	·956	·950	·946
40°	·993	·985	·978	·971	·963	·956	·949	·942	·934	·927
45°	·991	·981	·972	·962	·953	·944	·934	·925	·915	·906
50°	·988	·976	·964	·952	·939	·927	·915	·903	·891	·879

Table III.

*Pounds of water contained in 1,000 cubic feet of moist air at various degrees of humidity or percentages of saturation at various temperatures.*

The values are obtained from the equation—

$$W = \frac{18.03 \times p \times 1000 \times 273}{359 \times (273 + t)}$$

W being the weight required;  $p$  the partial pressure of the water vapour in atmosphere; 18.03 the molecular weight of water and 359 the lb. molecular volume of a gas at n.t.p. in cubic feet. (The values of W do not vary sensibly with the total pressure of the air).<sup>2</sup>

Temp. ° C.	Degree of Humidity or Percentage of Saturation.									
	10 %	20 %	30 %	40 %	50 %	60 %	70 %	80 %	90 %	100 %
0°	0.030	0.061	0.091	0.122	0.152	0.182	0.213	0.243	0.274	0.304
5°	0.042	0.084	0.126	0.168	0.210	0.252	0.293	0.335	0.377	0.419
10°	0.059	0.117	0.176	0.234	0.293	0.352	0.410	0.469	0.528	0.586
15°	0.080	0.160	0.240	0.320	0.400	0.480	0.560	0.640	0.720	0.800
20°	0.108	0.216	0.323	0.431	0.539	0.646	0.754	0.862	0.970	1.078
25°	0.144	0.287	0.430	0.574	0.718	0.861	1.004	1.149	1.291	1.436
30°	0.189	0.377	0.566	0.755	0.944	1.133	1.322	1.510	1.700	1.888
35°	0.246	0.493	0.739	0.985	1.232	1.478	1.724	1.970	2.215	2.463
40°	0.318	0.636	0.953	1.271	1.589	1.907	2.225	2.540	2.860	3.178
45°	0.407	0.815	1.222	1.630	2.037	2.445	2.850	3.260	3.665	4.074
50°	0.516	1.031	1.547	2.062	2.578	3.095	3.610	4.120	4.645	5.155

Table IV.

Pounds of water required to saturate 1,000 cubic feet of air of given initial humidity or percentage of saturation at a given constant temperature, the total pressure being kept at 1 atm.

Temp. ° C.	Initial Degree of Humidity or Percentage of Saturation.									
	0 %	10 %	20 %	30 %	40 %	50 %	60 %	70 %	80 %	90 %
0°	0.306	0.276	0.244	0.214	0.183	0.152	0.122	0.091	0.061	0.030
5°	0.423	0.380	0.337	0.295	0.252	0.210	0.168	0.126	0.084	0.042
10°	0.594	0.533	0.474	0.414	0.354	0.295	0.235	0.177	0.117	0.058
15°	0.814	0.731	0.650	0.567	0.485	0.404	0.322	0.241	0.161	0.080
20°	0.102	0.991	0.878	0.767	0.656	0.545	0.436	0.326	0.217	0.108
25°	1.481	1.330	1.178	1.028	0.879	0.729	0.582	0.436	0.289	0.145
30°	1.970	1.768	1.564	1.363	1.162	0.965	0.769	0.575	0.381	0.189
35°	2.603	2.328	2.060	1.791	1.528	1.266	1.007	0.750	0.579	0.249
40°	3.426	3.064	2.702	2.346	1.997	1.650	1.311	0.975	0.648	0.320
45°	4.495	4.010	3.528	3.058	2.596	2.140	1.698	1.262	0.831	0.413
50°	5.860	5.210	4.580	3.965	3.346	2.754	2.172	1.608	1.062	0.517

The figures in Table IV. are obtained as follows. The values for the amount of water required to saturate 1,000 cubic feet of unsaturated air of given initial humidity at a given constant temperature at constant volume are found from Table III. by subtracting from the value corresponding to 100 per cent. saturation at the given temperature, the amount corresponding to the given initial percentage of saturation at the same temperature. In practice, however, saturation will, as a rule, take place under the constant total pressure of 1 atm. instead of at constant volume. As the amount of water in saturated air at a given temperature depends on the volume only, irrespective of the partial pressure of the air itself, a correction must be applied to the above results to allow for the expansion accompanying saturation. The volumes before and after saturation at the given temperature, the total pressure remaining 1 atm., will be to each other in the inverse ratio of the corresponding partial pressures of the net dry air present. These partial pressures are given in Table II. To obtain the figures in Table IV. the differences obtained from Table III., as described above, are, therefore, multiplied by the initial partial pressure of the net dry air and divided by the partial pressure corresponding to saturation.

*Water required to saturate air when the temperature rises.*—This condition arises, for example, in the cooling of water by evaporation into a current of air which is initially cooler than the water. As before, it will be assumed that the total pressure remains 1 atm.

Let  $t_1$  be the initial temperature of the air.

$t_2$  be the final temperature of the air.

$W$  be the lbs. of water per 1,000 cubic feet of original air at temperature  $t_1$ .

$W$  be the lbs. of water per 1,000 cubic foot of air saturated at temperature  $t_2$ .

$p$  be the partial pressure of the net dry air in the original air assumed to have been warmed from  $t_1$  to  $t_2$  out of contact with water.

$P$  be the partial pressure of the net dry air in air saturated at  $t_2$ .

Starting with 1,000 cubic feet of air at  $t_1$  containing  $w$  lbs. of water, suppose the temperature to be raised from  $t_1$  to  $t_2$  out of contact with water. The volume will now be:

$$1000 \times (273 + t_2)/(273 + t_1) \text{ cubic feet}$$

$$\text{or } 1000 T_2/T_1 \text{ cubic feet;}$$

if  $T_2$  and  $T_1$  are the corresponding absolute temperatures, and the amount of water in 1,000 cubic feet at  $t_2$  will be—

$$w T_1/T_2 \text{ lb.}$$

As explained above, to saturate 1,000 cubic feet of air at temperature  $t_2$  containing, initially,  $w T_1/T_2$  lbs. of water, we require—

$$(W - w T_1/T_2) \times p/P \text{ lb. of water.}$$

Hence to saturate  $1000 T_2/T_1$  cubic feet at  $t_2$  we require in all—

$$(W - w T_1/T_2) \times \frac{p T_2}{P T_1} \text{ lb. of water.}$$

This operation may be simplified by using the tables. Thus by inspection of, or, if necessary, interpolation from Table III. we find that  $w T_1/T_2$  lb. of water in 1,000 cubic feet of moist air at  $t_2$  corresponds to some percentage of saturation  $h$ . By inspection of Table IV. we find at once the amount of water required to saturate 1,000 cubic feet of air of initial percentage of saturation  $h$  at  $t_2$ . This amount, which is:

$$(W - w T_1/T_2) \times p/P$$

in the above expression, when multiplied by  $T_2/T_1$  gives the answer.

*Example.*—Given 1,000 cubic feet of air measured at  $10^\circ$  C. and 1 atm., the degree of humidity or percentage of saturation of which at  $10^\circ$  is 70 per cent., how much water will be required to saturate this air at  $45^\circ$  C. and a total pressure of 1 atm., allowing for the increase of volume due to rise of temperature and evaporation of the water?

By inspection of Table III. we see that 1,000 cubic feet of air, 70 per cent. saturated at  $10^\circ$  C. contain 0.410 lbs. of water. If this air be heated to  $45^\circ$  C. out of contact with water, the volume will be increased to—

$$1000 \times 318/283 = 1,124 \text{ cubic feet;}$$

and the quantity of water per 1,000 cubic feet will be—

$$0.410 \times 283/318 = 0.365 \text{ lb.}$$

From Table III. it is seen that at  $45^\circ$  C. 0.365 lb. of water per 1,000 cubic feet corresponds with about 9 per cent. saturation; and by interpolation from Table IV. that to saturate 1,124 cubic feet of air of

9 per cent. initial percentage of saturation at 45°, the water required is 4.058 lb. Hence, to saturate the whole of the air, of which the initial volume at 45° in 1,124 cubic feet we require in all:—

$$4.056 \times 318/283 = 4.56 \text{ lb. of water.}$$

An inspection of Table III. shows that the amount of water evaporated will be small if the initial temperature of the air is above that of the water, even if the initial humidity of the air is as low as 50 per cent.

## SECTION II.

*Weight of water for unit weight of air.*—For tables giving lb. of water required to saturate 1,000 lb. of dry and moist air (or grams of water per kilogram of air) at various temperatures and pressure; also vapour pressure, density and specific volume of saturated water vapour see—

Landolt and Boernstein's Tabellen, pages 368 and 369.

Kent's Mechanical Engineers' Pocket Book, 9th Ed., pages 577 and 610 to 613.

For tables giving quantities of air at various temperatures and humidities required for a cooling tower, see:—

Kent's Pocket Book, pages 1080 and 1081.

The following table may be useful:

Table V.

*Lb. of water required to saturate 1,000 lb. of dry air at 1 atm. total pressure and various temperatures.*

Temp. C.	-	-	5°	0°	5°	10°	15°	20°	25°	30°
Lb. of water	-	-	2.6	3.8	5.5	7.7	10.7	14.8	20.5	28.1

## SECTION III.

*Heat absorbed by evaporation of water.*

Table VI.

*Latent heat of evaporation of water from Smith's formula—*

$$L = 597.2 - 0.580t \text{ C.H.U. per lb.}$$

t° C.	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°
L	597	594	591	588	585	582	580	577	574	571	568

*Specific heat of air.*

$$0.237 \text{ C.H.U. per lb. per } 1^\circ \text{ C.}$$

or  $0.237 \times 0.0807 \times 1,000 = 19.13 \text{ C.H.U. per 1,000 cubic feet at } 0^\circ \text{ C. and 1 atm. per } 1^\circ \text{ C.,}$

or  $19.13 \times \frac{273}{273+t} \text{ per 1,000 cubic feet at } t^\circ \text{ and 1 atm. per } 1^\circ \text{ C.}$





FEED REQUIRED-TONS PER DAY

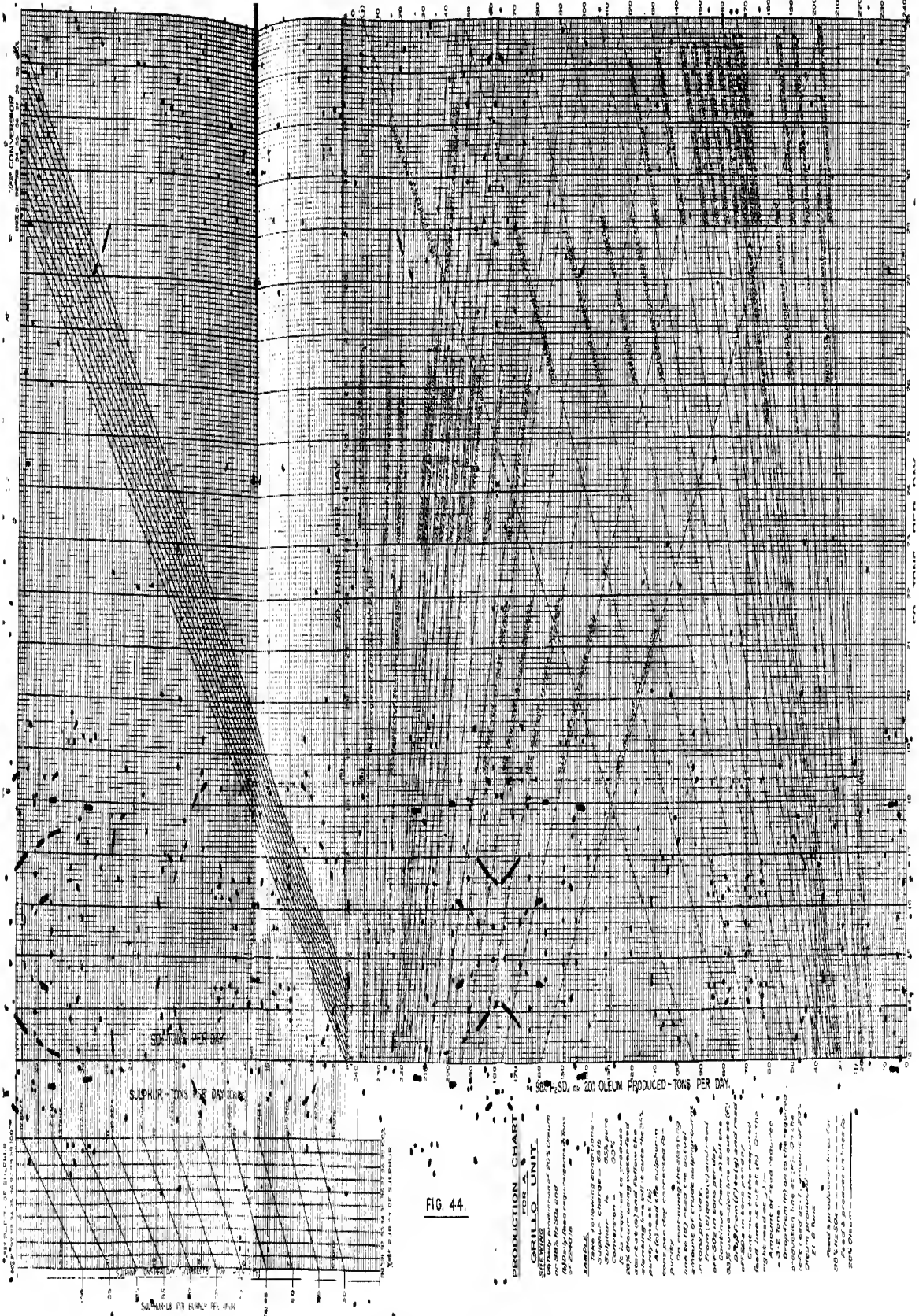


FIG. 44.

PRODUCTION CHART  
FOR A GRILLO UNIT.

NOTE: This chart is based on the following assumptions:  
1. The unit is operated at 100% efficiency.  
2. The unit is operated at 100% capacity.  
3. The unit is operated at 100% production rate.  
4. The unit is operated at 100% feed rate.  
5. The unit is operated at 100% sulfur production rate.  
6. The unit is operated at 100% sulfur consumption rate.  
7. The unit is operated at 100% sulfur feed rate.  
8. The unit is operated at 100% sulfur production rate.  
9. The unit is operated at 100% sulfur consumption rate.  
10. The unit is operated at 100% sulfur feed rate.

PRODUCTION CHART FOR A GRILLO UNIT.

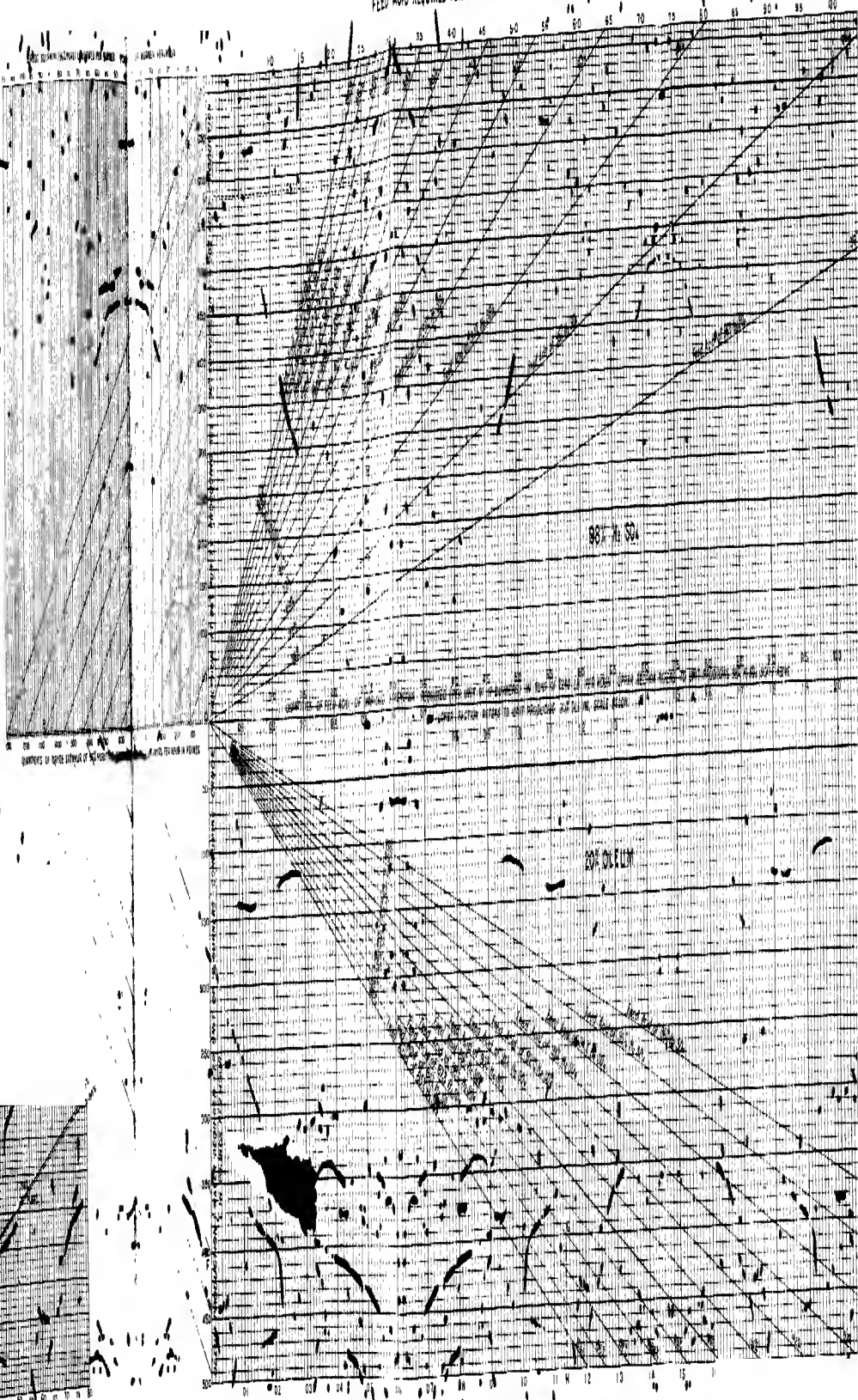
# FEED CHART FOR CONTACT PLANT

FEED ACID REQUIRED FOR THE PRODUCTION OF 98% H<sub>2</sub>SO<sub>4</sub> TONS OF 2240 LB. PER HOUR

## EXPLANATORY NOTES

Diagram shows—  
 1. Lines to left, the total quantities of 98% Sulphur  
 2. The amount per unit, per unit, when the quantities of  
 acid sulphur dioxide in the parallel are more or less  
 needed in each burner per hour  
 3. The amount of acid, with per unit, is  
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 99. The amount of acid, with per unit, is  
 100. The amount of acid, with per unit, is

② PRODUCING 98% H<sub>2</sub>SO<sub>4</sub>  
 Point A on line above shows 100% H<sub>2</sub>SO<sub>4</sub> is required to  
 be consumed of Sulphur. Follow the perpendicular  
 line to B where shows the total sulphur consumed per  
 unit. Then follow the diagonal to C which shows the  
 lbs of water per hour are required to feed 98%  
 acid from the unit. At D the amount of 98% con-  
 sumed. The horizontal line intersects the line for 98%  
 and across to E from which the perpendicular to F  
 takes the axis of "WATER" at G, showing that  
 17 tons of feed acid at 98% strength are required  
 or less.  
 The weight volume chart in the left hand lower  
 corner shows that 17 tons of acid at this strength  
 occupies 107 cubic ft per hour at 60°C.  
 ③ PRODUCING 20% OILUM  
 The course to follow will now be 20% OILUM, showing  
 100 tons of feed acid at 98% strength are re-  
 quired per hour.  
 The weight volume chart showing that this is equal  
 170 cubic ft per hour at 60°C.



FEED ACID REQUIRED FOR THE PRODUCTION OF 20% OILUM TONS OF 2240 LB. PER HOUR

FIG 43







